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Sulfonation of Eugenol-Diallyl Phthalate Copolymer as Base Material of Supercapacitor Electrode Material

Ngadiwiyana [1,*], Cinta Nur Nabila [1], Ismiyarto [1], Marcelinus Christwardana [1]

[1] Chemistry Department, Faculty of Sciences and Mathematics, Diponegoro University, Jl. Prof. Soedarto, SH., Tembalang, Semarang, Indonesia

* Corresponding author: ngadiwiyana@live.undip.ac.id

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Abstract

Polyeugenol is a polymer synthesized from renewable natural resources and has potential as a supercapacitor electrode material. Polyeugenol was modified by the addition of diallyl phthalate to increase structural density and thermal stability and the addition of sulfonate groups to increase ion exchange capacity and electrical conductivity. This research begins with the synthesis of eugenol-diallyl phthalate copolymer (PEGDAF) carried out by cationic polymerization using $BF_3O(C_2H_5)_2$ catalyst and sulfonation of eugenol-diallyl phthalate copolymer (SPEGDAF) using sulfuric acid. The synthesis of PEGDAF in the form of pink solids with a yield of 68.44%, a molecular weight of 6739.99 Daltons, and a melting point of 85°C, FTIR analysis showed that the formation of PEGDAF was characterized by the loss of vinyl groups with the absence of C=C alkene wavenumber absorption which is the wavenumber absorption of eugenol and diallyl phthalate, respectively 1640 cm^{-1} and 1647 cm^{-1} and TGA with a mass loss of 5% and 10% at 176°C and 219°C. SPEGDAF results in dark purple solids with a sulfonation degree of 17.18% and a cation exchange capacity of 0.4186 meq/g, molecular weight 8342.25 Daltons, melting point 114°C. Analysis using FTIR showed the presence of sulfonate groups with the resulting absorption peaks of 1218 cm^{-1} (S=O), 1065 cm^{-1} (S-O), and 578 cm^{-1} (C-S) and TGA with a mass decrease of 5% and 10% at temperatures of 169°C and 215°C. Potential test of supercapacitor electrode material with Cyclic Voltammetry and Electrochemical Impedance Spectroscopy obtained a specific capacitance value of 3.23×10^{-3} F/g and ion conductivity of 7.58×10^{-6} S/cm.

1. Introduction

Using natural resources in developing materials as energy storage is an interesting study today. One energy storage that is flexible but has high electrochemical properties is supercapacitors. Supercapacitors have the advantage of being charged and discharged in a short time, have a large energy storage capacity, high power density, and have a longer endurance cycle [1]. Supercapacitors consist of a current collector, electrolyte solution, and electrodes. Electrode materials used in supercapacitors include conductive polymers and metal oxides. Conductive polymers are an attractive option compared to metal oxides. This is because conductive polymers have a large specific capacitance value, low cost, and good electrical conductivity [2].

One conductive polymer with good conductivity and widely developed is sulfonated polystyrene [3]. Polystyrene is synthesized from petroleum, which can cause environmental problems such as greenhouse gas emissions and global warming [4]. Dwindling petroleum reserves and the resulting environmental impact encourage research to find solutions to replace petroleum with renewable natural resources, especially for the polymer industry, to be very interesting [5].

Polymers from renewable natural materials with a structure similar to polystyrene are polyphenols. Polieugenol has a phenolic functional group (-OH) that can conduct protons. Polieugenol has a disadvantage in the form of a high swelling degree that can cause crossover or instability in the copolymer [6]. The swelling degree value can be reduced through modification of the polymer structure with the addition of crosslinks, and this modification can also improve material stability and maintain electrode performance during charge and discharge cycles [7]. The crosslinker used is diallyl phthalate because it can increase the density of the structure and good tensile strength [6]. The addition of diallyl phthalate as a cross-linker is expected to increase the thermal resistance of the resulting polymer to support the performance of supercapacitor electrode materials.

In addition to swelling degree and thermal resistance, the material requirements for use as supercapacitor materials include proton transfer capability, ion conductivity, and specific capacitance. The ability of eugenol-diallyl phthalate copolymer (PEGDAF) as the basic supercapacitor material can be improved by adding sulfonate group (-SO_3H), a strong acid. The sulfonation process is carried out using a sulfonation agent in the form of sulfuric acid. The addition of sulfonate groups is expected to increase ion conductivity and cation exchange capacity to increase the ability of PEGDAF to conduct electricity [6, 8].

This research is expected to contribute to developing renewable and environmentally friendly supercapacitor materials derived from natural resources. This research is also expected to increase the utilization and value of eugenol and clove oil, which are abundant natural resources in Indonesia.

2. Experimental

2.1. Instrumentation and Materials

The instrumentation used were Fisher-John melting point apparatus, blonde viscometer, Cary 630 FTIR Spectrometer, Thermogravimetric Analyzer (TG7300), and PalmSens4 Electrochemical Impedance Analyser/Potentiostat/Galvanostat. The materials used were eugenol (for synthesis, Merck), diallyl phthalate (Merck), $BF_3O(C_2H_5)_2$ (Merck), chloroform (Merck), methanol (Merck), ethanol (Merck), dichloromethane (Merck), ethyl acetate (Merck), diethyl ether (Merck), tetrahydrofuran (THF) (Merck), acetone (Merck), distilled water, anhydrous Na_2SO_4, 98% H_2SO_4, NaCl 0.1 M, NaOH 0.02 M, PP indicator, universal pH, filter paper, sandpaper, copper plate (3 cm × 10 cm), and aluminum foil.

2.2. Synthesis of Eugenol-Diallyl Phthalate Copolymer (PEGDAF)

The synthesis of the PEGDAF followed the modified procedure outlined in [6]. PEGDAF was synthesized using 65 mmol (10.03 mL) of eugenol and 6.5 mmol (1.427 mL) of diallyl phthalate in a molar ratio of 10:1, respectively. This mixture was placed into a three-neck flask equipped with a reflux circuit and maintained under a nitrogen (N_2) gas flow. A $BF_3O(C_2H_5)_2$ catalyst (4 mL) was slowly added using a dropper funnel over seven and a half hours. After the addition, the reaction mixture was left to stand overnight. To terminate the polymerization reaction, 2 mL of methanol was added. Upon addition, the solution thickened, and its color changed from yellow to purple.

The resulting polymer was dissolved in 50 mL of diethyl ether and then neutralized by washing with distilled water ten times until the pH reached neutrality. Using a separating funnel, the diethyl ether solution containing the polymer was separated from the water layer. The neutral pH of the water layer was confirmed, and the diethyl ether was evaporated in a desiccator to obtain the polymer. The dried polymer was then ground into a powder.

Characterization of the PEGDAF included molecular weight determination using the Mark-Houwink equation with an Ubbelohde viscometer, assessment of physical properties (melting point and solubility), functional group analysis with FTIR, and thermal resistance evaluation using TGA-DTG

2.3. Sulfonation of Eugenol-Diallyl Phthalate Copolymer (SPEGDAF)

The sulfonation of the PEGDAF was performed following a modified procedure outlined in [6]. Four grams of the PEGDAF were dissolved in 60 mL of chloroform in a glass beaker and stirred until homogeneous. The resulting solution was transferred to a three-neck flask and refluxed at 60°C. Sulfuric acid (1.6 mL, 0.03 mol) was added to the solution, which was then stirred for two hours under inert conditions. After the reaction, cold distilled water was added to the solution to form two layers, which were separated using a separating funnel. The pH of the water layer was measured, and the remaining polymer layer was evaporated in a desiccator. The dried polymer was ground into a powder.

Characterization of the sulfonated eugenol-diallyl phthalate copolymer (SPEGDAF) included the following: determination of molecular weight using the Mark-Houwink equation with an Ubbelohde viscometer; assessment of physical properties (melting point and solubility); determination of the degree of sulfonation and cation exchange capacity; functional group analysis with FTIR; and thermal resistance evaluation using TGA-DTG.

2.4. Potential Test of Supercapacitor Electrode Material

The procedure for testing the potential of supercapacitor electrode materials was to measure the specific capacitance and ion conductivity of the electrode.

2.4.1. Preparation of Electrode Materials with Sulfonated Eugenol-Diallyl Phthalate Copolymer

The electrode coating with SPEGDAF was carried out following a modified procedure outlined in [9]. Copper plates (3 cm × 10 cm) were prepared by polishing with sandpaper, then cleaned sequentially with distilled water, acetone, and distilled water again. The plates were dried at room temperature. The coating solution was prepared by dissolving 1 gram of SPEGDAF in 2.5 mL of tetrahydrofuran in a vial bottle and stirring the mixture with a magnetic stirrer for 90 minutes. The prepared solution was then applied to the copper plates by drop-casting for two dips. The coated plates were left to dry at room temperature overnight.

2.4.2. Electrode-Specific Capacitance Measurement

The specific capacitance of the electrode was measured using cyclic voltammetry with a Rodeostat, following a modified procedure outlined in [10]. The measurements were conducted using a three-electrode system comprising a SPEGDAF as the working electrode, a platinum (Pt) plate as the counter electrode, and an Ag/AgCl electrode as the reference. The electrolyte was KCl at a concentration of 0.05 M, with a scan rate set to 0.05 mV/s. Data acquisition was performed continuously until the completion of the test. The specific capacitance was calculated using Equation (1).

$$C_{sp} = \frac{A}{2.m.k.(V_1 - V_2)} \qquad (1)$$

Where, C_{sp} is the specific capacitance (F/g), V_1 is the anodic (oxidation) potential (V), V_2 is the cathodic potential (reduction) (V), k is the scan rate (mV/s), m is the electrode mass (g), and A is the surface area (A.s).

2.4.3. Electrode Ion Conductivity Measurement

The ion conductivity of the electrode was measured using Electrochemical Impedance Spectroscopy (EIS) with a PalmSens4 Electrochemical Impedance Analyzer, following a modified procedure outlined in [10]. The measurements were conducted using a three-electrode system comprising a SPEGDAF as the working electrode, a Pt plate as the auxiliary (counter) electrode, and an Ag/AgCl electrode as the reference. The electrolyte used was KCl at a concentration of 0.05 M. Nyquist plot data was generated using Origin software and fitted to a suitable model. Ion conductivity was calculated using Equation (2).

$$\sigma = \frac{I}{RA} \qquad (2)$$

Where, σ is the conductivity ($S.cm^{-1}$), I is the thickness (cm), R is the resistance (Ohm), and A is the surface area (cm^2).

3. Results and Discussion

3.1. Synthesis of Eugenol-Diallyl Phthalate Copolymer (PEGDAF)

PEGDAF was synthesized under inert conditions by flowing with N_2 gas. The formation of the PEGDAF through a cathodic addition polymerization reaction consists of three stages: initiation, propagation, and termination. The initiation stage involves the formation of carbocations, marked by a color change in the solution from yellow to pink. The propagation stage follows, during which the carbocations react with other monomers to generate new carbocations. This process continues, leading to the formation of long polymer chains, which are characterized by the solution becoming viscous. Finally, the termination stage occurs when methanol is added to stop the copolymerization, resulting in the polymer solidifying. The reaction mechanism of the PEGDAF is illustrated in Figure 1.

The dried PEGDAF product is a pink solid with a yield of 68.44%. The solubility test revealed that the copolymer is soluble in methanol, ethanol, dichloromethane, ethyl acetate, and chloroform but insoluble in distilled water. The melting point was determined to be 85°C, with a molecular weight of 6739.99 Daltons. Functional group analysis of the eugenol-diallyl phthalate copolymer, performed using FTIR and presented in Figure 2, confirmed the formation of the copolymer. This was indicated by the loss of vinyl groups, evidenced by the absence of C=C alkene absorption bands at 1640 cm^{-1} and 1647 cm^{-1}, corresponding to the wavenumbers of eugenol and diallyl phthalate, respectively. The disappearance of these bands indicates that the vinyl groups underwent an additional reaction to form the copolymer. Evidence of cross-linking in the copolymer, attributed to diallyl phthalate, is observed through the presence of a C=O ester absorption band at 1722 cm^{-1}. Comparative FTIR absorption data for eugenol, diallyl phthalate, and the PEGDAF are summarized in Table 1.

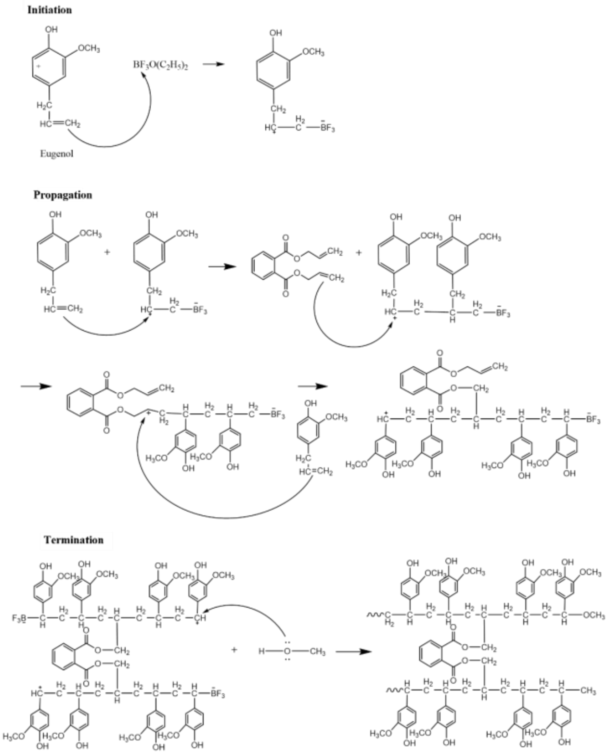

Figure 1. Reaction mechanism of eugenol-diallyl phthalate copolymerization

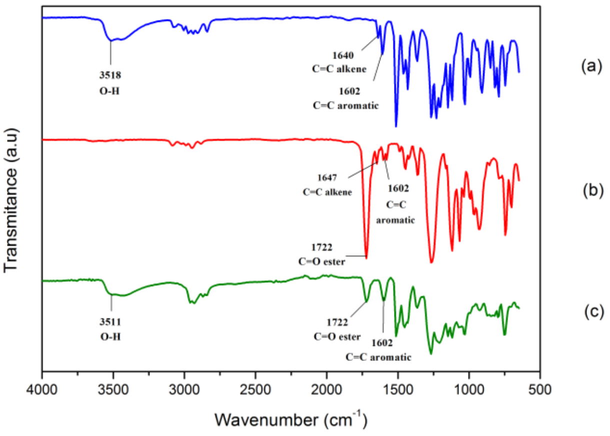

Figure 2. FTIR spectra of a) eugenol, b) diallyl phthalate, and c) PEGDAF

Table 1. Comparison of functional groups and wavenumbers of eugenol, diallyl phthalate, and PEGDAF

Functional group	Wavenumber (cm^{-1})		
	Eugenol	Diallyl phthalate	PEGDAF
OH stretching	3518	-	3511
C-H sp^3 stretching	2974	2944	2959
C=C aromatic	1610	1602	1602
C-H sp^3 bending	1453	-	1453
C-O ether stretching	1233	1267	1207
C=C alkane stretching	1640	1647	-
C=O ester stretching	-	1722	1722
C-O ester stretching	-	1259	1267

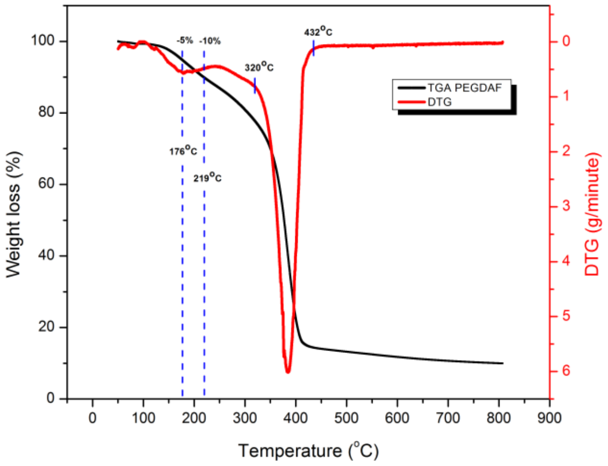

Figure 3. TGA-DTG curve of PEGDAF

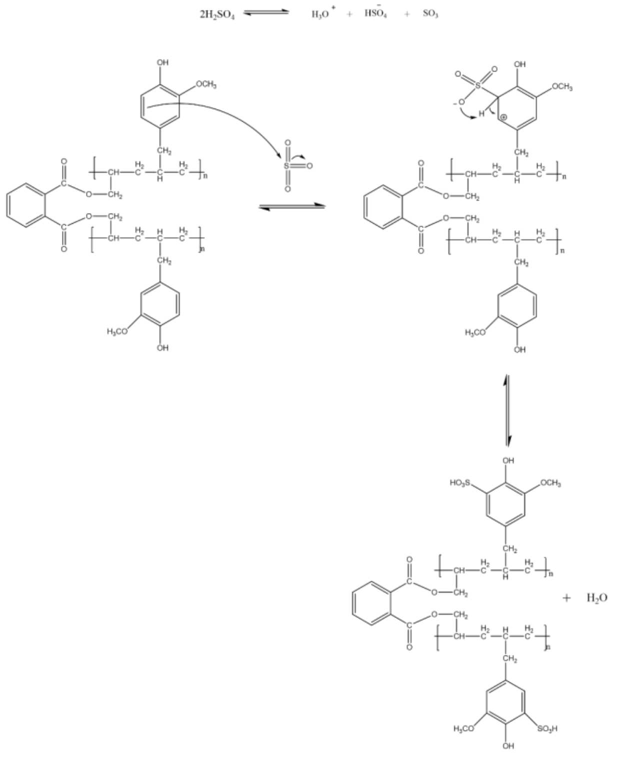

Figure 4. Sulfonation reaction of PEGDAF

The thermal resistance of the PEGDAF was analyzed using TGA-DTG. Polyeugenol exhibited a mass loss of 5% and 10% at 75°C and 186°C, respectively [11]. In contrast, the PEGDAF showed a mass loss of 5% and 10% at 176°C and 219°C, respectively. These results indicate that polyeugenol has lower thermal resistance than the eugenol-diallyl phthalate copolymer, making the latter a more suitable coating material [12]. The TGA-DTG analysis of the PEGDAF is shown in Figure 3.

3.2. Sulfonation of Eugenol-Diallyl Phthalate Copolymer (SPEGDAF)

The addition of sulfonate groups to the PEGDAF resulted in the formation of the SPEGDAF. The purpose of introducing the sulfonate group is to enhance the ion conductivity of the copolymer. The sulfonation reaction of the PEGDAF with concentrated sulfuric acid as the sulfonating agent is shown in Figure 4. The SPEGDAF obtained is a dark purple solid. Solubility tests revealed that the sulfonated copolymer is soluble in methanol, ethanol, ethyl acetate, chloroform, and dichloromethane but insoluble in distilled water. The melting point increased from 85°C to 114°C, while the molecular weight increased from 6739.99 Daltons to 8342.25 Daltons.

The degree of sulfonation, which indicates the average number of sulfonate groups (-SO_3H) per polymer chain, was measured using an acid-base titration method, as described in the previous study [13]. The SPEGDAF was soaked in NaCl solution, where Na^+ ions substituted H^+ ions in the sulfonate groups, leading to the production of HCl. The amount of HCl generated was used to determine the concentration of sulfonate groups in the copolymer. The degree of sulfonation of the SPEGDAF was 17.18%.

The success of the sulfonation process can be assessed by the degree of sulfonation, where a polymer with a sulfonation degree greater than 40% is soluble in water due to the enhanced ionic properties of the sulfonate groups, which also increase the polymer's conductivity [14]. The reaction mechanism for determining the degree of sulfonation using NaCl is shown in Figure 5.

Table 2. Comparison of functional groups and wavenumbers of PEGDAF and SPEGDAF

Functional group	Wavenumber (cm^{-1})	
	PEGDAF	SPEGDAF
OH stretching	3511	3503
C-H sp^3 stretching	2959	2958
C=C aromatic	1602	1604
C-H sp^3 bending	1453	1459
C-O ether stretching	1207	1218
C=O ester stretching	1722	1717
C-O ester stretching	1267	1244
S=O stretching	-	1218
S-O stretching	-	1065
C-S stretching	-	578

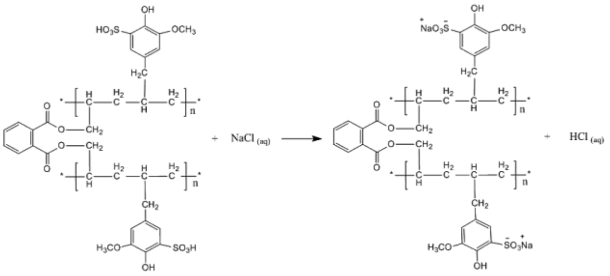

Figure 5. Sulfonation reaction of PEGDAF with NaCl

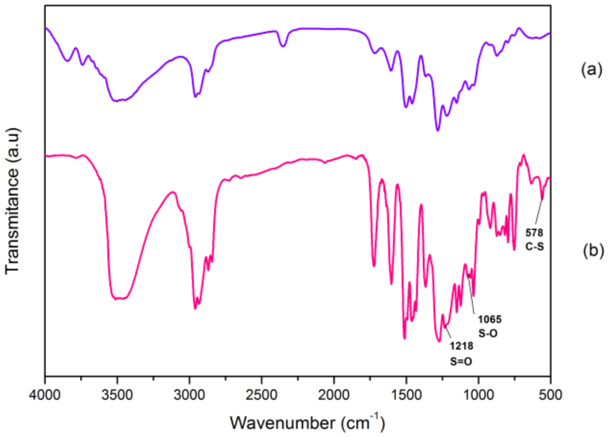

Figure 6. FTIR spectra of a) PEGDAF and b) SPEGDAF

The degree of sulfonation is directly proportional to the cation exchange capacity. Cation exchange capacity measures a polymer's ability to exchange cations bound to its functional groups with cations in the surrounding system. In this case, H^+ ions are the cations in the functional group, while Na^+ ions are the cations introduced into the system. The cation exchange capacity increases with the degree of sulfonation. A polymer with a higher degree of sulfonation will more easily release H^+ ions, resulting in a higher cation exchange capacity.

In supercapacitors, polymers must have a high cation exchange capacity. The greater the cation exchange capacity, the higher the ionic conductivity, which in turn enhances the polymer's ability to conduct electricity [6]. The cation exchange capacity of the SPEGDAF was determined to be 0.4186 meq/g. The presence of sulfonate groups in the PEGDAF was confirmed through FTIR analysis, as shown in Figure 6. The difference between the spectra of PEGDAF and SPEGDAF is characterized by the presence of sulfonate groups. The resulting absorption peaks for the sulfonated copolymer are 1218 cm^{-1} (S=O), 1065 cm^{-1} (S-O), and 578 cm^{-1} (C-S). A comparison of the spectra of PEGDAF and SPEGDAF is provided in Table 2.

Based on Table 2, the S=O group and C-O ether (from sulfonation) show a wavenumber at 1218 cm^{-1}. This is due to the overlap of the S=O group with the C-O ether. A deconvolution of the FTIR spectra in the wavenumber range of 1150–1250 cm^{-1} was performed to confirm sulfonation. The deconvolution results, shown in Figure 7, reveal the addition of derivative peaks in the FTIR spectra of the sulfonated eugenol-diallyl phthalate copolymer. Peak II corresponds to the presence of the bound S=O group. The deconvolution produced two distinct absorption peaks: in peak I, there is a C-O ether at 1229 cm^{-1}, and in peak II, there is S=O at 1212 cm^{-1}. The PEGDAF produces an absorption at 1228 cm^{-1} for the C-O ether.

The transmittance of the C=C benzene group absorption is used as a standard to calculate the %transmittance before and after sulfonation, as no change in absorption occurs at this peak. The %transmittance before sulfonation was 0.97, and after sulfonation, it decreased to 0.88. This indicates a higher concentration of spectral groups after sulfonation. According to Beer-Lambert's law, concentration is inversely proportional to transmittance. The observed increase in concentration, as shown by the S=O group in the sulfonated eugenol-diallyl phthalate copolymer, confirms that sulfonation was successfully carried out.

The TGA-DTG analysis of the SPEGDAF is shown in Figure 8. The PEGDAF experienced a mass loss of organic compounds by 5% and 10% at 176°C and 219°C, respectively. In contrast, the SPEGDAF showed mass losses at 169°C and 215°C. The thermal stability of the SPEGDAF decreased due to the degradation of the sulfonic acid groups [6]. Sulfonic groups tend to increase the polarity of the polymer, which in turn decreases its thermal stability, causing the sulfonated polymer to degrade at lower temperatures [15].

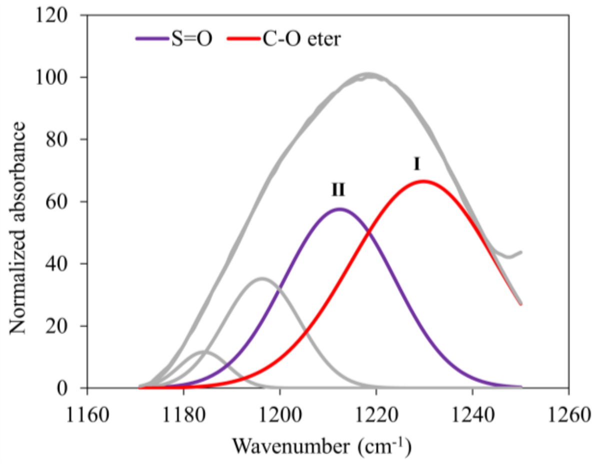

Figure 7. Deconvolution of FTIR spectra of SPEGDAF (1250-1150 cm⁻¹)

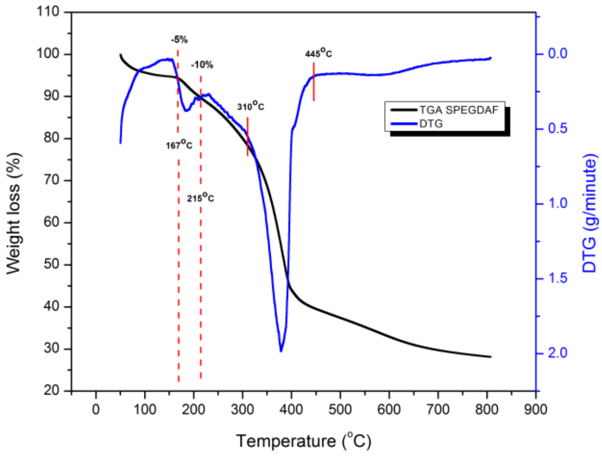

Figure 8. TGA-DTG curve of SPEGDAF

3.3. Potential Test of Supercapacitor Electrode Material

3.3.1. Specific Capacitance of Electrode

Specific capacitance measurement of sulfonated eugenol-diallyl phthalate copolymer-based electrodes was tested using cyclic voltammetry. The electrolyte solution was KCl 0.05 M with a scan rate of 0.05 mV/s. The measurement results are shown in Figure 9.

Based on Figure 9, SPEGDAF has a larger surface area than polyeugenol and PEGDAF. The greater the surface area of a material, the greater the ability to absorb and release charges efficiently, which can increase the specific capacitance in supercapacitors to store more energy [16]. This is evidenced by the specific capacitance graph in Figure 10.

Based on the specific capacitance graph, polyeugenol exhibited a value of 1.58×10^{-3} F/g, PEGDAF 1.67×10^{-3} F/g, and SPEGDAF 3.23×10^{-3} F/g. The higher capacitance of SPEGDAF is consistent with its greater cation exchange capacity value. This suggests that the higher the cation exchange capacity, the higher the specific capacitance, which in turn enhances the polymer's ability to conduct electricity [6]. The specific capacitance values of supercapacitor electrode materials typically range from 5.844×10^{-9} to 2700 F/g [17]. This confirms that SPEGDAF qualifies as a suitable material for supercapacitor electrodes.

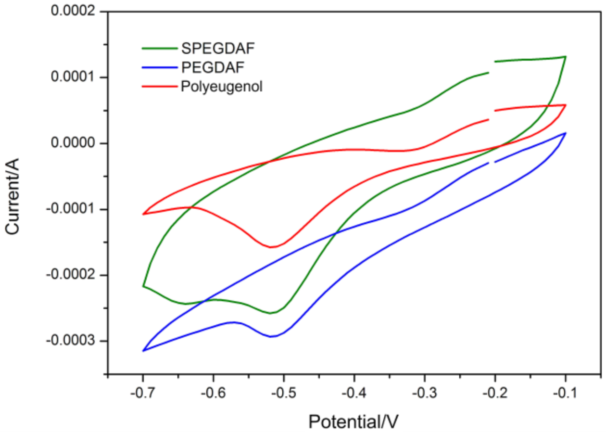

Figure 9. Cyclic voltammogram of polyeugenol, PEGDAF, and SPEGDAF

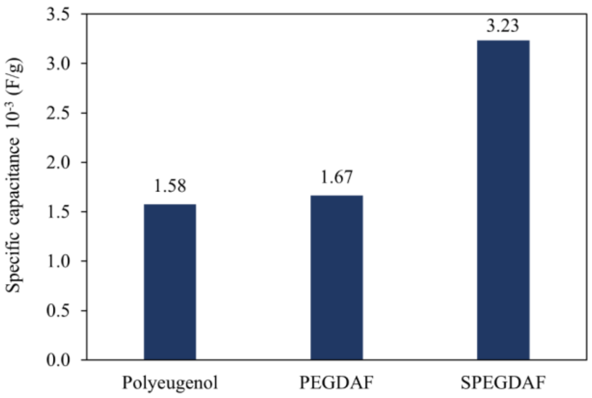

Figure 10. Specific capacitance graph of polyeugenol, PEGDAF, and SPEGDAF

3.4. Ion Conductivity of Electrodes

Ion conductivity measurements of SPEGDAF-based electrodes were tested using Electrochemical Impedance Spectroscopy (Figure 11). The electrolyte resistance (R_s) and charge transfer resistance (R_{ct}) values of polyeugenol, PEGDAF, and SPEGDAF are presented in Table 3.

Changes in electrolyte resistance and charge transfer resistance from polyeugenol to PEGDAF did not change significantly due to the addition of ester groups while there was a significant decrease in SPEGDAF due to the presence of sulfonic groups which are strong acids that produce rapid ion transfer between the electrode and electrolyte. The low electrolyte resistance and charge transfer resistance can increase ion conductivity as well as during charging and discharging [17]. This is evidenced by the ion conductivity measurement results in Figure 12.

Table 3. R_s and R_{ct} values of polyeugenol, PEGDAF, and SPEGDAF

Material	R_s (ohm)	R_{ct} (ohm)
Polyeugenol	28.47	36.5
PEGDAF	23.07	33
SPEGDAF	15.68	23

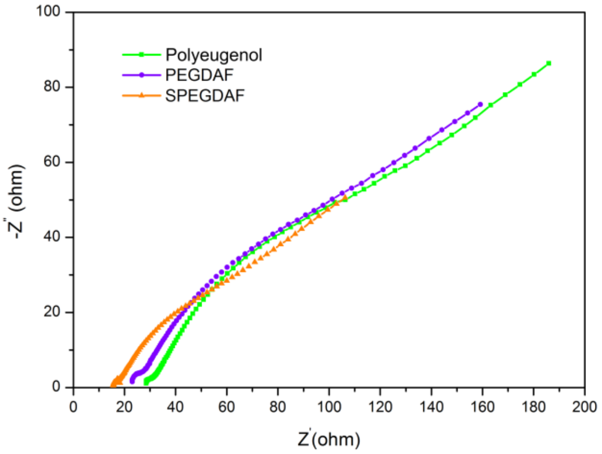

Figure 11. EIS graph of polyeugenol, PEGDAF, and SPEGDAF

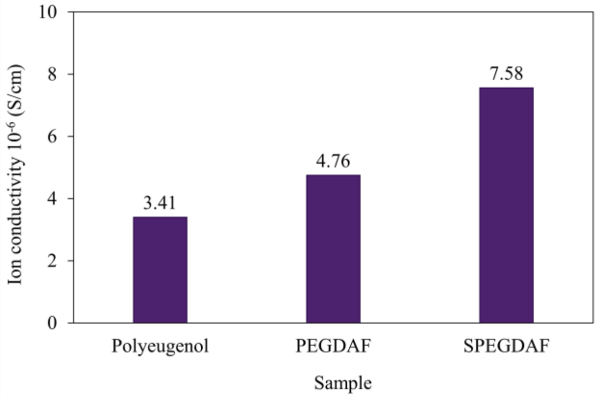

Figure 12. Ion conductivity graph of polyeugenol, PEGDAF, and SPEGDAF

Based on Figure 12, the ion conductivity values of polyeugenol, PEGDAF, and SPEGDAF are 3.41×10^{-6} S/cm, 4.76×10^{-6} S/cm, and 7.58×10^{-6} S/cm, respectively. The increase in ion conductivity is influenced by the degree of sulfonation; the higher the degree of sulfonation, the greater the ion conductivity [6]. A material is considered a semiconductor if its conductivity falls within the range of 10^{-8}–10^{3} S/cm [18]. Previous research [19] reports an ion conductivity value of 1.5×10^{-7} S/cm, which is lower than the ion conductivity of SPEGDAF at 7.58×10^{-6} S/cm. This demonstrates that the SPEGDAF material exhibits superior ion conductivity, making it a better superconducting material.

4. Conclusion

The synthesis of PEGDAF successfully produced a pink solid with a yield of 68.44%, a melting point of 85°C, and a molecular weight of 6739.99 Daltons. TGA analysis revealed a mass loss of 5% and 10% at 176°C and 219°C, respectively. Sulfonation of the PEGDAF resulted in a dark purple solid with a melting point of 114°C and a molecular weight of 8342.25 Daltons. The degree of sulfonation was 17.18%, and the cation exchange capacity was 0.4186 meq/g. TGA analysis of the sulfonated copolymer showed a mass loss of 5% and 10% at 169°C and 215°C, respectively. The SPEGDAF demonstrated potential as a base material for supercapacitor electrodes, with a specific capacitance value of 3.23×10^{-3} F/g and ion conductivity of 7.58×10^{-6} S/cm.

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