Potency of Carrageenan as the doping agent for poly(3,4-ethylenedioxythiophene) conductive polymer

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Abstract. Poly(3,4-ethylene dioxythiophene) (PEDOT) is a highly electronic material. PEDOT is an insoluble polymer, but it can be an aqueous dispersion in polystyrene sulfonate (PSS) solution as the doping agent. Carrageenans are anionic heteropolysaccharide with ester sulphate groups, which are similar functional group contained in PSS. Carrageenan, one of the potentials natural source of Indonesia, are structured of alternating β-d-galactopyranose and 3,6-anhydrogalactose or α-d-galactopyranose. Carrageenans are possible potential as the alternative doping agent for PEDOT to prepare PEDOT/Carr dispersions due to their similarity on –SO3- functional group. This study prepared PEDOT/Carr aqueous dispersion in 1:1 ratio by weight as a conductive green polymer. PEDOT/Carr (1:1) dispersion was succesfully synthesized by oxidative polymerisation via in-situ and post-polymerisation reaction. The effect of base solutions or pH is very interesting to investigate on physicochemical of carrageenan doped with PEDOT. Processable conductive PEDOT/Carr dispersion needs to be investigated to optimize the properties of the film.

1. Introduction
Poly(3,4-ethylene dioxythiophene) (PEDOT), one of the derivates of polythiophenes, has been attracting specific attention due to its electronic properties including its synthesis, application, and additional doping agent (dopant). PEDOT is a black and highly valuable electric material. It is insoluble in many organic and inorganic solvents, but it can be an aqueous dispersion in the presence of polyelectrolyte polystyrene sulphonate (PSS) as the charge balancing doping agent [1]. Doping PEDOT and PSS in PEDOT/PSS dispersion can be facilitated by the presence of –SO3H functional group which is hydrophilic part and make it soluble in water. In this case, the unpaired electron on the PEDOT chain will be highly mobile along the backbone making it highly conductive. Stability and processability of PEDOT/PSS aqueous dispersion are better in performing film such as high in conductivity, visible light transparency, and also excellent in stability of the film [2, 3].

The commercially available PEDOT/PSS aqueous dispersions have low conductivity [4, 5]. Many researchers investigate PEDOT/PSS in order to improve the properties, such as the conductivity and solubility. We have studied to synthesize PEDOT at a different time of reactions and ratio of EDOT
and PSS as the dopant and resulted in better conductivity [6-8]. We have learned statistically conductivity of the films produced from the PEDOT/PSS commercially available [9]. Some researchers have used various additives to achieved improvement on electronic properties of PEDOT/PSS films [10, 11]. The conductivity of PEDOT/PSS films enhanced recently 1880 times that was achieved by pristine film using additional DMS [12], and higher than 2000 S/cm by treating with ionic liquid[13], and 3000 S/cm with H₂SO₄ [14]. Some additional dopants to PEDOT/PSS aqueous dispersions have been used and described in detail [15].

Another natural polyelectrolyte with ester sulfate groups is carrageenan. Thus similarity of this functional group makes carrageenan interesting to investigate its potency as a dopant for PEDOT. Indonesia is the largest exporting country from seaweed farming for producing carrageenan. Most cultivated seaweeds from Indonesia based primarily of Kappaphycus (cottonii), Eucheuma (spinosum), and Gracilaria. These are sources of the hydrocolloids and well known as agar, κ- and ι-carrageenan, respectively [16].

Carrageenan is a naturally anionic sulfated linear polyelectrolyte generated by extraction of red seaweeds (Rhodophyta)[17], and mainly from the species Gigartina, Chondrus crispus, Eucheuma and Hypnea[18]. These polysaccharides are also produced in Indonesia as cultivated seaweeds farming. Carrageenan is composed of alternating β-d-galactopyranose (G-units), and 3,6-anhydrogalactose (DA-units), or α-d-galactopyranose (D-units). In general, there are seven basic forms of carrageenan, i.e lambda (λ), iota (ι), kappa (κ), nu (ν), mu (μ), and theta (θ), and ksl (ξ)-carrageenan. All forms contain about 22–35% of sulfate groups[18]. Thus from this similarity on this sulfate group, it is possible for carrageenan as the alternative dopant for PEDOT to make processable PEDOT/Carr dispersions which are potential for film with good properties, better conductivity and light transparency.

Many routes are possible for the synthesis of PEDOT from EDOT monomer. In the structure of EDOT, the oxygen bonded to the 3- and 4-positions of the thiophene ring, minimize unwanted polymerization reaction at these β-carbon sites. In addition, these oxygens act as the electron-donating group, which will increase the capacity of an electron in the thiophene ring[19]. In general, PEDOT derivatives can be synthesized through three different types of reactions: oxidative chemical polymerization as the most popular, electrochemical polymerization and transition metal-mediated coupling of EDOT[20]. The oxidative polymerization can be processed using a number of methods and oxidants. Nevertheless, the classical method used iron (III) chloride (FeCl₃)[20]. The resulting black powder of PEDOT could be precipitated from the mixture as it is insoluble in organic solvents and water.

Synthesis of PEDOT aqueous dispersions with PSS as the doping agent has been discussed[3, 6-8, 21]. PEDOT/PSS aqueous dispersion can be synthesized by oxidative polymerization of the EDOT monomer in PSS solution and using oxidizing agent Na₂S₂O₈ and Fe₂(SO₄)₃ in water. This reaction generates PEDOT segments which are dispersed in aqueous medium by forming PEDOT/PSS complexes. Figure 1 exhibits that the positively charged of PEDOT segments in this complex are tightly doped to PSS (negatively charged). The PEDOT segments are believed to be shorter molecular weight than PSS with previous reports indicating 5-10[4], and 5-15[22], 6-18[1], repeating units.

![PEDOT Oligomer](image)

**Figure 1.** The structure of PEDOT/PSS complex[1, 4, 6-8].

Various and expanding uses of PEDOT/PSS dispersion have been discussed in detail for more than three decades, and currently many applications of PEDOT/PSS films include an anticorrosive additive
for paints[23], and as cathodes active material in battery[24]. This polymer has also been used for antistatic coating [21], and drug delivery applications[25], biosensing[26], and, PEDOT/PSS as the blend is also useful for electronic device such as for organic photovoltaic devices (OPVs)[5], organic field effect transistors (OFETs)[27], and organic light emitting diodes (OLEDs)[28]. The use of highly conductive PEDOT is advisable to replace inorganic materials.

This paper deals with the potenti possibility of κ-carrageenan as one of the source of doping agent for conductive polymer poly(3,4-ethylenedioxythiophene) or PEDOT in aqueous dispersion (PEDOT/Carr). Synthesis of PEDOT/Carr is very interesting because solubility of carrageenan is depending on the concentration of sulphated fraction, which is hydrophilic and correlated to cationic reaction [29]. The number of sulphate groups and the anhydrous parts in carrageenan structures affect their properties. The dimers of κ-carrageenan consist of one sulphate ester groups. This dimer is equal for corresponding contents of about 20% (w/w) amounted sulphate [30]. In general, commercial carrageenans have various molecular weight, ranging from 400 to 700 kDa [31]. These are potential back bond for doping PEDOT segment. Some studies mentioned that carrageenan exhibited various effects on biological and chemical activities. Therefore, they are possible as for promising green polymers application.

2. Research Method

2.1 Materials
κ-carrageenan, 3,4-Ethylenedioxythiophene (EDOT), Na₂S₂O₈, Fe₂(SO₄)₃, and NaOH were purchased from Sigma-Aldrich Australia and used as received. PEDOT/PSS Clevios P was purchased from H.C. Starck (Munich, Germany). Acidic and basic ion-exchange resins (LEWATIT, Bayer AG) were purchased from Sigma-Aldrich Australia. Methanol (MeOH) was used as received from the supplier. Dialysis tubes, Membra-Cel Dialysis Membranes MWCO 3500, were purchased from SERVA.

2.2 Preparation of PEDOT/Carr aqueous dispersion via oxidative polymerization (in-situ addition of Carrageenan)
The procedure for the synthesis of PEDOT/Carr aqueous dispersion was modified from the general procedure of the synthesis of PEDOT/PSS aqueous dispersion as previously described by Diah, et al [8]. Typically, 384.5 mg of κ-carrageenan diluted in 50 ml of water at 65 °C and keep the solution on the pH ≈ 8. After stirring overnight, 389.0 mg of 3,4-ethylenedioxythiophene was mixed to the solution to obtain a 1:1 ratio of the PEDOT/Carr by weight. A 388.5 mg of Na₂S₂O₈ initiator was then added and the reaction mixture made up to 60.0 mL with RO water. After stirring for 10 minutes, 6 mg of Fe₂(SO₄)₃ was added and the reaction mixture was stirred vigorously for 24 h of reaction. The dark blue aqueous mixture was purified by stirring with acidic, then basic ion exchange resins (~500 mg) about 10 minutes. Solutions then dialyzed in methanol and water to remove the unreacted monomers and oxidation agents. Dialysis allowed removal excess of H⁺ and maintained the dispersions neutral.

2.3 Post-polymerisation addition of Carrageenan
PEDOT was synthesized in water according to the procedure outlined in Section 2.2 in the absence of κ-carrageenan. The resulting dried polymer was then mixed with an appropriate amount of κ-carrageenan solution at 65 °C and the pH > 8 to obtain a PEDOT/Carr ratio of 1:1 by weight and stirred vigorously overnight (24h) to provide the PEDOT/Carr aqueous dispersions. Purification of the solution was performed as previously described using resins and dialysis tube.

2.4 Characterisations
PEDOT/Carr aqueous dispersions were characterized physically using microscope “Axioskop 40 Pol” from ZEISS. Structures were analyzed using FTIR. FTIR spectra were recorded as neat samples on a Perkin Elmer Spectra Two ATR FTIR. The spectra bands were recorded in the range of 4000 to 500 cm⁻¹.
3. Results and Discussion

3.1 Synthesis of PEDOT/Carr aqueous dispersions
There were two procedures to synthesis PEDOT/Carr aqueous dispersion in this study. The first synthesis was by in-situ polymerization, Where all reactants such as EDOT monomer, oxidation agents, and carrageenan were synthesized as PEDOT/PSS [7, 8] with some modification conditions. Temperature and acidity of the solution were set up at 65 °C and pH > 8 prior polymerization reaction. As the κ-carrageenan will be gelation in room temperature and κ-carrageenan will be hydrolyzed on an acidic solution [31]. The second procedure was by post-polymerization PEDOT by the additional κ-carrageenan solution. The synthesis was started by synthesis PEDOT, then the addition of κ-carrageenan as the dopant. Both procedures followed the PEDOT/Carr dispersions in 1:1 ratio by weight.

The synthesis of PEDOT/Carr in situ in the presence of κ-carrageenan via oxidative polymerization was carried out using Na$_2$S$_2$O$_8$ and Fe$_2$(SO$_4$)$_3$ as the oxidation agents in water at 65°C for 24 h. An indication of the progress of the reaction was observed from the change in the color of the solution (to dark blue), indicating the formation of PEDOT, as shown in figure 2A and 2B. The acidity of the solution after the reaction was ~3 indicating that the carrageenan was possibly hydrolyzed and became poligeenan which have lower molecular weight. The excess of EDOT monomer, oxidation agents, and acid or basic ions were purified using dialysis tube (MWCO 3500) in methanol and continued in water as performed in previous studies [7, 8]. The dark blue PEDOT/Carr dispersion synthesized in situ precipitated after 2 h polymerization process (see figure 3A) while by post-polymerization was still in dark dispersion. This precipitation indicated the stability of the dispersion with in situ process was less stable than post-polymerization addition of carrageenan. This is also possible lower molecular weight of the doping agent (poligeenan instead of carrageenan) due to hydrolysis process. Therefore, PEDOT segment doped with short molecular weight polyelectrolyte and showed as unstable dispersion.

Figure 2. Synthesis PEDOT/Carr in-situ polymerization at 0 h reaction (A), and after 24 h reaction (B).

Figure 3. PEDOT/Carr (1:1) solutions two hours after ion exchanging with resins: by in-situ polymerization (A) and by postpolymerization addition Carrageenan (B).

3.2 Characterisation of PEDOT/Carr aqueous dispersions
The successful synthesized PEDOT/carr aqueous dispersion was identified using FTIR spectra recorded by a Perkin Elmer Spectra Two ATR FTIR. Figure 4 shows the FTIR spectra of the
PEDOT/Carr both synthesized in situ and postpolymerization films, the EDOT monomer, and the commercial κ-carrageenan, respectively. The spectra band at 892 cm\(^{-1}\) due to the C-H bending on EDOT disappeared in PEDOT/Carr demonstrating successful formation PEDOT chains.[32] The band at 1481 and 1366 cm\(^{-1}\) are attributed to the stretching modes of C=C and C-C in the thiophene ring, whereas bands at 1205 and 1058 cm\(^{-1}\) are due to the stretching mode of the ethylenedioxy group from C-O-C bond stretching, respectively. Figure 4 also presents the spectra of κ-carrageenan by appearing of very strong absorption bands in the around 1226 cm\(^{-1}\) region (due to the S = O of sulphate esters) and 1036 cm\(^{-1}\) region (as the glycosidic linkage). A particular signal was recorded at 925 cm\(^{-1}\), which is specific to 3,6-anhydro-D-galactose. Another signal was identified at 842cm\(^{-1}\) (attributed to D-galactose-4-sulfate).[33, 34] The FTIR spectrum of PEDOT/Carr films both synthesized in situ and post polymerisation addition κ-carrageenan are shown similar peaks attributing of the groups containing in both samples consistent with the EDOT monomer and κ-carrageenan.

![FTIR spectra of PEDOT/Carr film, EDOT monomer, and κ-carrageenan.](image)

The representative surface morphology images of PEDOT/Carr films produced by drop casting have also been observed by optical microscopy (see figure 5A and 5B). PEDOT/Carr film from the in-situ reaction was very rough and not homogenous surface. The very rough film was possible presumably due to short chains of the polygeenan resulted from hydrolysis of carrageenan doped with PEDOT segment. However, the surface of the film from post-polymerization PEDOT by additional κ-carrageenan is less rough but still wavy. Both films are found some lumps and aggregations formed during drying of the films observed appearing as white patches. These patches are presumably due to aggregation of Carrageenan or polygeenan occurred during drying of PEDOT/Carr film. Similarly, the representative surface morphology image of commercial PEDOT/PSS as the comparison (see figure 5C), the film shows more homogeneous and uniform. The morphology image also exhibits some patches on the surface as can be seen in the other films presumably due to aggregation of PSS,[5] which occurred during drying of PEDOT/PSS film. These representative images can be cahallenged for carrageenan as te dopant of PEDOT to repalace polystyrene sulfonic acid (PSS).
Figure 5. The morphology images of PEDOT/Carr (1:1) films produced via in-situ polymerization (A) and postpolymerization addition Carrageenan (B) compare with commercial PEDOT/PSS film (C). Images were taken using microscope “Axioskop 40 Pol” from ZEISS in 20x magnification.

Carrageenan are usually used in industry of foods such as for stabilizing, gelling, thickening, improving textures and controlling textures of foods, and also in pharmaceutical, textiles, cosmetics, and printing industries [29, 31, 35, 36]. In addition, Carrageenan also has no nutritional value and have been discussed for further improvement in various applications for dairy and non-dairy food [29]. They are cost-effective materials for some purposes applications in food and non-food industries. The extensively used of carrageenan was also reported in a combination with other materials containing carboxymethyl as the promising application as conductive green polymer electrolyte [37]. The data in this study indicate the possibility of carrageenan as a new one of natural polyelectrolyte for doping agent with PEDOT conductive polymer.

4. Conclusion
Overall, κ-carrageenan is a natural anionic heteropolysaccharide containing ester sulphate groups, which is similar functional group contained in PSS. κ-carrageenan has been successful to end-capped PEDOT via oxidative polymerisation as evident from the spectra analyses (FTIR). κ-carrageenan shows as an alternative as another doping agent for PEDOT to make processable PEDOT/Carr dispersions which are potential enough as for good film-forming properties, i.e high conductivity, and visible light transparency. Then the use of highly conductive PEDOT doped carrageenan is advisable as an alternative for replacing inorganic materials. Processability of PEDOT/Carr dispersion needs to be studied in advance from the aspect of preparation and properties of synthesis including the properties of the film and their application.

Acknowledgments
The authors would like to thank Tadulako University (Palu, Indonesia), The University of Newcastle Australia, and the Directorate of Research and Community Service (DRPM), Ministry of Research and Higher Education of the Republic of Indonesia for the research funding support in 2018 (097/SP2H/LT//DRPM/2018).

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