Effect of PVDF composition in activated carbon derived from chicken feather on electrical properties

E Hastuti1* and I Irfana1
1Department of Physics, Universitas Islam Negeri Maulana Malik Ibrahim Malang
Jl Gajayana 50 Malang, Indonesia
*Email : erna@fis.uin-malang.ac.id

Abstract. Chicken feathers are agricultural wastes and become pollutants because of the resistance to protease degradation. Feathers contain a fibrous protein called keratin and potentially for producing activated carbon. In many applications, activated carbon is made of composites with poly (vinylidene fluoride) PVDF to improve its function. This research was carried out to study the effect of PVDF composition on activated carbon derived from chicken feathers on electrical properties. Besides evaluating changes in chemical structure and surface morphology, composites were tested using FTIR and digital microscopy. An addition of PVDF improves its dielectric properties. But the higher composition, causing agglomeration that inhibits polarization. The dielectric constant and conductivity of composite with 15 wt% PVDF are 1950 and 1.45 x 10^{-5} S/cm at 1 kHz, larger than another composition.

1. Introduction
Energy storage becomes important due to the increasing demand for electrical power supply for mobile devices. Electrochemical energy storage technologies have an advantage because of their possible use in high power applications. Supercapacitors and batteries are typical electrochemical energy conversion and storage devices which store electricity in electrochemical processes [1]. The electrode material is an important component in energy storage performance. Recently, widely developed are electrodes from carbon, and mainly the utilization of waste and agro-industrial resources [2]. Carbon materials derived from biomass precursors, including activated carbon, porous carbon, and nanostructured carbon with high conductivity, rich porosity, and the potential to improve electrodes performance for energy storage [3].

Animal-based biomass presence of a higher concentration of nitrogen, sulfide, and another chemical composition than plant/fruit-based biomass. Besides chitin in crustaceans (crab, shrimp, lobster), keratin in the hair, horn, claw, and feather of animals is also a good precursor for producing carbons [4]. Keratin consists of strong intermolecular bonding, including covalent disulfide cystine crosslinking, ionic salt bonds, and non-covalent hydrogen bonds [5]. Keratin can be obtained from chicken feathers. Chicken feathers are the major waste from poultry industry, disposed of in lands, and causing environmental issues [6]. The chemical composition shows that it is composed of 91% keratin protein, with β-sheet structure and small amount of α-helices [7]. After carbonization and activation using KOH, keratin can allow a uniform structured microporous material and possesses a surface area of 1839 m²g⁻¹ [8].

In its use as an electrode, activated carbon is mixed with a polymer that functions as a binder. Binder, electrode materials, and its composition play an important role in energy storage. Homogeneity and surface interactions affect electrode performance because energy stored electrostatically on the surface
of material and does not involve the chemical reactions [9]. Poly (vinylidene fluoride) (PVDF) is used as binder material that has properties of non-reactive and non-toxic thermoplastic fluoropolymer with high molecular weight, high dielectric constant, excellent film-forming property and good flexibility, high chemical corrosion resistance and good heat resistance [10]. PVDF has a variety of polymorphs like α-(TGTG), β-(TTTT), and γ-(TTTGGT') phases and gained extensive investigated by many research groups and are considered to be promising materials for applications in a variety of fields [11].

In this present work, activated carbon derived from chicken feather was synthesized through pyrolysis and activated using KOH 5M. The activated carbon blended with PVDF in various compositions (i.e., 5, 10, 15 and 20 wt%) to form a composite. The materials were characterized in terms of surface chemistry and electrical properties to obtain the optimal composition.

2. Experimental

2.1. Preparation of activated carbon derived from chicken feather
In this work, chicken feather used as a starting precursor for producing activated carbon (AC). The dried chicken feather was carbonized at 215 °C for 15 hours, and then at 450 °C for an hour in a vacuum. After smashed in mortar and sieved by the griddle (150 mesh), the powder was soaked in 5M KOH solution for 24 hours at room temperature. Subsequently, the slurry was washed with 1 M HCl and distilled water and followed by activation at temperature 950 °C for 3 hours in air atmosphere.

2.2. Composites preparation
The matrix material is a Polyvinylidene fluoride, [(CH₂-CF₂)n] granules (RM 4439) were obtained from Hi-Media Laboratories. For preparation of AC/PVDF composites, PVDF was first dissolved in DMSO (Dimethyl sulfoxide) at 90 °C. Then, different amount of AC was added to the well-dispersed solution under stirring. The mixtures were mechanically stirred about 80 °C for an hour to form a homogeneous dispersion. Following mixing, each sample poured into a mold and heated at 100 °C to remove residual solvent.

2.3. Characterization
Surface functional groups and structure of activated carbon and AC/PVDF composites were studied by FTIR (FT 1000 Varian). The measurements were carried out at a resolution of 2 cm⁻¹, and a wavenumber range from 400 to 4000 cm⁻¹ to obtain spectra lines. Investigation of the character of activated carbon distribution in PVDF was performed for all composites using digital microscope and processed using ImageJ software. Electrical properties (dielectric constant, dielectric loss, and conductivity) of composites in the frequency ranging from 100 Hz to 5 MHz were measured at room temperature by LCR meter (HIOKI 3532-50, HiTester). The silver paint was applied on both composites surface and then dried about 50 °C to act as electrodes.

3. Result and Discussion
The functional groups of activated carbon and PVDF were identified using FTIR (Figure 1). As can be seen in Figure 1, all of spectra show absorption band at around 3850, 3750-3650, and 665 cm⁻¹. The position of bands are characteristics of the vibration of C=O ketones, CH-R aldehydes, and C-S sulfide, that identified as keratin [7]. The presence of keratin can also be inferred from C=O stretching in the amide I at 1640 cm⁻¹, and N-H bending in the secondary amide (1540-1515 cm⁻¹). This Amide I and amide II are related with β-sheet structure in the chicken feather [12]. Furthermore, the band at 1455 and 1390 cm⁻¹ indicates the stretching vibration of the C=C and C–H bonds in carboxyl groups, respectively. The presence of small peak around 2920 and 2300 cm⁻¹ can be assigned to C-H stretching vibration and have been attributed to amino acids in keratin [13]. The wide peak at 3400 cm⁻¹ confirms hydroxyl –OH functional group in the activated carbon [14].

In the FTIR spectra of the composite samples, it is verified that characteristic peaks referred to PVDF, as shown in Figure 1(b-e). The vibration around 840 cm⁻¹ corresponds to C-H stretching frequency,
which refers to the stretch of β-phase of PVDF. Peaks at 560, 870, and 1170 cm\(^{-1}\) refer to the stretching of CF\(_2\) bond that presents in the polymer chain of PVDF [15]. The FTIR spectrum also shows the increase of C-F bond at 1170 cm\(^{-1}\) that proves a higher concentration of PVDF. The β phase of PVDF affects the electrical conductivity of composites.

Figure 1. FTIR spectra of AC/PVDF composite.

The following figures show optical microscope of the surface of composite materials AC/PVDF with various compositions (figure 2). The optical microscope observations revealed the homogeneous distribution and large porosity for small PVDF (below 10 wt%), which is due to the small amount of PVDF as a binder. An addition of PVDF concentration enhancing interfacial interaction between AC and PVDF. On samples with PVDF concentrations above 10 wt% present agglomeration and become larger at 20 wt% PVDF. This large agglomeration decreases interfacial interactions and affects the electrical properties of composites [16].

Figure 2. Photographs (a-d) and ImageJ analysis (e-h) of AC/PVDF composite.

The electrical properties of AC/PVDF composites were measured between operating frequency 500 Hz to 5MHz at room temperature. The frequency-dependent dielectric constant of composites is shown in Figure 3. Figure 3 describes addition of PVDF up to 15 wt% improves the dielectric constant of the composite. At a frequency of 1 kHz, the dielectric constants are 1510, 1730, and 1950 for 5, 10, and 15...
wt% PVDF, respectively. The enhancement in the dielectric constant of composite represents the interfacial interaction of activated carbon and PVDF. The dielectric constant of the composite is mainly determined by the electric polarization of the activated carbon.

An addition of PVDF shows dipole polarization of the PVDF matrix faces an enhancement. Under the electric field effect, the interfacial polarization occurs due to the number of activated carbon atoms interaction to the PVDF surface [17]. The larger the number of PVDF is, the stronger polarization and the greater the dielectric constant of the composites are. The PVDF molecular chains with β phase have high dipole moment due to alignment of all dipole chains in a single direction. The CH₂/CF₂ configuration orientation produces high spontaneous polarization and makes PVDF excellent property for piezoelectric, pyroelectric, and ferroelectric film [16]. However, at composite with 20 wt% PVDF, the dielectric constant significantly decreases, up to 122. This composition declined dielectric constant due to the agglomeration of PVDF, so their interaction with active carbon is reduced [18]. This agglomeration was shown in the results of a digital microscope (Figure 2).

![Figure 3. Dielectric constant of AC/PVDF composite](image1)

![Figure 4. Dielectric loss of AC/PVDF composite](image2)

Besides, the dielectric constant at activated carbon with 5, 10, and 15 wt% PVDF decreases significantly with increasing frequency. At higher PVDF, the dielectric constant decreases smoothly in this range. The dipole moment tends to align itself with the direction of the field, resulting in polarization. But at high frequency, decreased due to dipole polarizability could not follow the insulated field's movement. In the oscillation of electric field, dipole experiences friction and collide with other molecules, while the ability of the material to convert electrical energy into heat energy known as dielectric loss.

Further discussion of the dielectric loss is shown in figure 4. As seen in the figure, there are no significant differences in dielectric loss factor in PVDF composition. When the PVDF composition is 10 wt%, dielectric loss at low frequency is lower than other composites. This value may be associated with the dipole polarization of PVDF and the leakage current between the activated carbon. The dielectric loss factor for all compositions decreases sharply with an increase in frequency. It can be mentioned that with the increasing frequency, the dipoles get very less time to orient themselves in the direction of an applied electric field. Therefore, dielectric constant and loss factors decrease with an increasing frequency for all composites [18].

Further, PVDF composition on composite AC/PVDF shows change of conductivity, as shown in figure 5. The maximum electrical conductivity of composite with 15 wt% PVDF addition is 1.45x10⁻⁵ S/cm at 1 kHz, which indicates a rather good insulation characteristic of the composite. The conductivity values were slightly different on the PVDF composition of 5 and 20 wt%, which approaches 1.3x10⁻⁵ S/cm and 1.1x10⁻⁵ S/cm, respectively. However, in composite with PVDF 10 wt%, conductivity of
composite shows significant differences. This conductivity decreases obviously at low frequencies, is about \(3.7 \times 10^{-6}\) S/cm, and increases sharply at high frequencies. In comparison, the conductivities of composites with PVDF 5, 15, and 20 wt% loadings grow slowly with the increasing frequency up to \(10^5\) Hz. Then, the conductivity increases rapidly at frequency above \(10^5\) Hz, referred to as the electronic polarization effect.

![Conductivity of AC/PVDF composite](image)

**Figure 5.** Conductivity of AC/PVDF composite.

Increasing the composition of PVDF can enhance charged carriers in electric field and reduce interparticle distance between activated carbon and PVDF, thereby improving the conductivity of composite. In contrast, more agglomeration at composite with PVDF 20 wt% causing longer distance from each other, which provided resistance to the electron mobility and caused a decrease of conductivity.

4. Conclusion

In conclusion, activated carbon fabricated from chicken feather waste by carbonization and activation with KOH. PVDF added as a binder affects the characteristics of the composite. The surface functional groups confirm that the PVDF in the composites has a \(\beta\) phase. This phase causes an enhanced in the dielectric constant and the conductivity of the composite. Activated carbon/PVDF with 15 wt% showed significant increase in the dielectric constant value of 1950 and conductivity of \(1.45 \times 10^{-5}\) S/cm at 1 kHz. Besides, electrical properties of composites are also determined by homogeneity and interfacial interaction between activated carbon and PVDF. At 20 wt% PVDF composition, agglomeration is formed and causes a decrease in dielectric constant to 122.

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