Frequency dependence of electrical properties of polyvinylidene fluoride/graphite electrode waste/natural carbon black composite

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Abstract. Polyvinylidene fluoride (PVdF) is a semi-crystalline thermoplastic material with remarkably high piezoelectric coefficient and an attractive polymer matrix for micro-composite with superior mechanical and electrical properties. The conductive filler is obtained from Graphite Electrode Waste (GEW) and Natural Carbon Black (NCB). The variation of composite content (%) of PVdF/NCB/GEW were 100/0/0, 95/5/0, 95/0/5, 95/2.5/2.5. This experiment employed dry dispersion method for material mixing. The materials were then moulded using hot press machine with compression parameters of $P = 5.5$ MPa, $T = 150$ °C, $t = 60$ minutes, $A = 5 \times 5 \times (0.2 - 0.4)$ cm$^3$. The electrical conductivity properties of pure PVdF, as well as PVdF/GEW, PVdF/NCB, and PVdF/NCB/GEW composites were investigated in a frequency range of 100 to 100000 Hz. The PVdF/GEW sample obtained the highest electrical conductivity. It is concluded that GEW and NCB can be incorporated into PVdF as a conductive filler to increase the conductivity of conductive material composite without solvent.

1. Introduction

The Waste-to-Energy (WtE) technologies can be applied for various type of waste (e.g. semi-solid, liquid, and gaseous waste from the effluent of treatment industry or medium factory). These technologies deal with waste treatment process that generates energy in form of electricity, heat, transports fuels or composite material for energy devices [1].

The carbon black (CB) can be obtained from the decomposition of biomass waste, such as coconut fibers which are abundant and easy to obtain. Natural carbon black (NCB) decomposition occurs usually at a temperature corresponding to the thermodynamic conditions of the precursor to form charcoal, including by-products such as tar and gases [2]. Graphite is a carbonaceous material; expanded graphite (EG) with a high aspect ratio and excellent electrical conductivity can be produced by exfoliating graphite intercalation compound (GIC) through rapid heating in a furnace or microwave environment. Graphite electrode waste (GEW) from electric arc furnace (EAF) can substitute graphite synthetic as a reinforcement material for carbon composite.

Composites material has been used widely in industrial sectors as materials for antistatic, electromagnetic shielding, and electronic technology [3, 4]. In electronic technology, composites material has been used for a device with improved electromagnetic and energy storage system (ESS) [5] or electrochemical energy storage systems (EESS) [6].
Polyvinylidene fluoride (PVdF) is a highly non-reactive and pure thermoplastic fluoropolymer material. Below 150 °C, PVdF becomes ferroelectric. Thus, PVdF is electro-active and semi-crystalline polymer with pyro and piezoelectric properties at room temperature, which can be used for many applications [7]. It exhibits high mechanical strength, good chemical resistance and thermal stability, as well as excellent aging resistance [8]. Moreover, PVdF is an attractive polymer matrix for composite material with superior mechanical and electrical properties.

The performance of conducting polymer composite depends on filler concentration which determines the electrical properties. However, higher filler content can lead to poor process ability and low mechanical properties. EG reinforced-conducting polymer composites have shown substantial improvements in electrical conductivity and mechanical property when CB is incorporated [9].

In this study, the electrical properties of PVdF with addition of some additives (e.g. GEW from the EAF and NCB from coconut fiber) are investigated. In addition, the effect of solvent in the process is also studied.

2. Experimental
The main material is commercial-grade PVdF powder (182702-2506), supplied by Sigma-ALDRICH Inc., USA. Meanwhile, NCB powder from coconut fiber and GEW powder from iron or steel smelting factory are used as an additive. GEW has particle size of < 44 μm. GEW from the EAF was chosen as a reinforcement material for electrically conductive material due to its similarity with synthetic graphite. Structural examination of GEW from the EAF showed the crystalline carbon structure, instead of amorphous structure, which implies its good conductivity [10].

Preparation of carbon materials, NCB powder was conducted in two main steps, namely carbonized and pyrolysis process. In the carbonization, process, coconut coir was carbonized at 500 °C temperature for an hour in a furnace with nitrogen atmosphere. Subsequently, the charcoal was pyrolyzed at 1300 °C temperature for an hour. NCB with particle size of < 44 μm was used as filler. Composite content (%) variation of PVdF/NCB/GEW were 100/0/0, 95/5/0, 95/0/5, and 95/2.5/2.5. Dry mixing or non-solvent method was used for material mixing. The waste of GEW/NCB/PVdF was mixed with a ball mill for 900 minutes, dried, and molded used compression hot press machine at 5.5 MPa pressure and 150 °C temperature for 60 minutes with 5×5×(0.2-0.4) cm³ dimension. Total weight composition to make raw material of carbon composite polymer is 20 gram. HIOKI 3522-50 LCR
HiTESTER was used to measure AC electrical conductance of the composite materials sample with frequency ranged from 100 to 100000 Hz.

3. Results and discussion

This experiment was meant to study the behaviour and electrical properties of PVdF/GEW/NCB Composite. PVdF/GEW/NCB is designed from graphite electrode waste and carbon black material developed from natural resource, in which the content is abundant and the process feasible. Carbonization step of coconut coir was performed to degrade the chemical compound of the coconut coir and produce charcoal. In order to reach activated conductive carbon, the charcoal was then pyrolyzed. One of the advantages of this processed is the simplicity [11].

Figures 2 - 4 display the frequency dependence of electrical properties. For PVdF/5 wt.% GEW, there is a transition from an insulator to semiconductor. GEW was chosen as a reinforcement material for electrically conductive material because it has the characteristics and specifications similar to synthetic graphite. The insulator-conductor translation is also confirmed by the large dissipation factor (tan δ) for PVdF/5 wt.% GEW (figure 2).

Figure 2. Frequency-dependence of the loss tangent of material composite.

The electric permittivity, energy loss, and dielectric relaxation strength are important parameters for material science because these parameters are used to decide on the suitability for given application. Measurement of AC electrical properties of the composite materials sample employed following formula.

The frequency dependence complex dielectric permittivity \( \varepsilon^*(\omega) \) is given by

\[
\varepsilon^*(\omega) = \varepsilon'(\omega) - i \varepsilon''(\omega)
\]

Here, \( \varepsilon'(\omega) \) and \( \varepsilon''(\omega) \) are the real and imaginary part of complex dielectric permittivity. PVdF/5 wt.% GEW as a function of frequencies at room temperature is shown in figure 3. As expected, the variation tendency of dielectric constant with frequency is inversely proportional to electrical conductivity (\( \sigma \)). The \( \varepsilon' \) attains high value at low frequency and decreases exponentially with increasing frequency.

Dielectric permittivity was measured with applied field at a frequency of 100 Hz to 100000 Hz. PVdF is dielectric material which stores charges. Dielectric properties also depend on the orientation of the structure in the material. Dielectric loss of permittivity can be calculated from the measured loss tangent and capacitance:

\[
V_\theta = V_x \sin(\pi - \varnothing)
\]
\[
\tan \delta = \left( \frac{V_T^2 - V_0^2}{V_0} \right)^{\frac{1}{2}}
\]

(3)

Figure 3. Frequency-dependence of dielectric constant of material composite.

The variation of conductivity (\(\sigma\)) at room temperature with frequency for different filler content (pure PVdF, PVdF/5 wt.% NCB, PVdF/5 wt.% GEW, and PVdF/2.5 wt.% NCB/2.5 wt.% GEW) of composites is shown in figure 4a and 4b at room temperature. Using dry mixing method, the electrical conductivity is fairly constant when the NCB and GEW load the content. Such composite materials generally exhibit non-linear increase of the electrical conductivity as a function of the filler concentration. The two parameters, electrical conductivity and percolation threshold, are together associated with. At a certain filler loading fraction, known as the percolation threshold, the fillers form a network leading to a sudden rise in the electrical conductivity of the composites.

The addition of a very low amount of conducting particles can make filler contact to form effective conducting paths and thus making the whole composite conductive. These specimens show a typical insulating behaviour with a frequency-dependent conductivity. However, the higher NCB loading in the polymer composite can cause serious NCB aggregation, and the electrical conductivity will lower or even decrease. Figure 4 shows electric conductivity of PVdF/2.5 wt.% NCB/2.5 wt.% GEW composites decreased due to the loading of NCB equal to the loading of GEW is in 2.5 wt.%. This occurs because the loading of NCB between the GEW particles does not act as a bridge for the mobility of electrons in any direction and does not provide gives electrical conductivity to the composite. Conductivity (\(\sigma\)) was calculated according to the relation:

\[
\varepsilon'(\omega) = \frac{C}{\varepsilon_0} \frac{d}{A}
\]

(4)

\[
\varepsilon''(\omega) = \varepsilon' \tan \delta
\]

(5)

Where, \(d\) is separation distance between two electrodes, \(A\) is electrodes area, \(\varepsilon_0\) is the permittivity of the free space, \((\varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m})\).

\[
\sigma = \varepsilon_0 \omega \varepsilon''
\]

(6)

Where \(\omega = 2\pi f\) is the angular frequency.

Figure 5 shows the electrical conductivity properties of pure PVdF, PVDF/5 wt.% NCB, PVdF/5 wt.% GEW, PVdF/2.5 wt.% NCB/2.5 wt.% GEW at frequency of 100 - 100000 Hz. The electrical
conductivity was enhanced the most in PVdF/5 wt.% GEW, i.e. at $1.26 \times 10^{-7}$ S.cm$^{-1}$. However, graph exhibited decreasing value of electrical conductivity in PVdF/2.5 wt.% NCB/2.5 wt.% GEW, i.e. at $9.81 \times 10^{-8}$ S.cm$^{-1}$.

Figure 4. Plot of frequency-dependence of electrical conductivity of material composite (left) and frequency-dependence of log electrical conductivity (right).

Figure 5. The electrical conductivity of varied composite content.

4. Conclusion and future work
Electrical properties of composite materials based on PVdF/5 wt.% NCB, PVdF/5 wt.% GEW, PVdF/2.5 wt.% NCB/2.5 wt.% GEW prepared by dry mixing were investigated depending on filler concentration, frequency, and deformation. The experimental results demonstrated that the investigated composites had some peculiarities of electrical properties in comparison with pure PVdF. The dielectric permittivity of PVdF/5 wt.% GEW composites was significantly higher than that of composites based NCB fillers. In addition, composites filled with GEW demonstrated the most stable electrical properties depending on such important exploitation parameters as deformation. This preparation method allows us to achieve a uniform distribution of filler in a polymer matrix and specific properties of filler particles. It makes GEW as alternative conductive filler for conductive material in electronic applications.
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