Preparation of Graphite Electrode Waste/Natural Carbon Black/Polyvinylidene Fluoride Composites Using Liquid Nitrogen Cold Quenching

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Abstract. Graphite and carbon are attractive carbon-carbon (C/C) composite materials for applications due to exceptional electrical transport properties and high charge mobility. The liquid nitrogen cold quenching method could increase porous, hardness, and electrical conductivity. Composite material graphite electrode waste/natural carbon black/polyvinylidene fluoride (GEW/NCB/PVDF) was made by mixing 70wt% GEW, 10wt% NCB and 20 wt% PVDF with non-solvent method by means ball mill for 900 minutes. The mixture was then moulded using hot press machine at pressure of 5.5 MPa, temperature of 150ºC for 60 minutes with dimension of $5 \times 5 \times 0.3$ cm$^3$. After that, put it off into liquid nitrogen quickly. The conclusion is preparation of GEW/NCB/PVDF composite by using liquid nitrogen cold quenching could increase porous, hardness, and electrical conductivity. However, this composite shows decrease in density.

1. Introduction

The development of material carbon-carbon (C/C) composite is important because they combine carbon-fiber reinforcement in all carbon matrix or materials in which two or more constituents have brought together to produce a new material nominally [1, 2]. Graphite and carbon are attractive C/C composite materials due to exceptional electrical transport properties, such as high conductivity and high charge mobility, have incredibly broadened the range of potential applications of this class of materials; thus unleashing a revolution in the electronic device industry [3, 4], and can be used as the electrical composite for power plant components [5]. Conducting C/C composites reinforced with thermoplastic polymer have shown substantial improvements in electrical conductivity [6].

Graphite electrode waste (GEW) from electric arc furnace (EAF) can substitute graphite synthetic as a matrix material for C/C composite. This GEW can be derived from the remnants of the smelting in production of steel in electric arc furnaces industry that is not used anymore. In addition, they are highly graphitic, exhibiting anisotropic optical texture, and capable for carrying a heavy electrical current at high temperatures under a large thermal stress. The natural carbon black (NCB) can be obtained from the decomposition of organic substances of biomass natural waste, such as coconut fibers, which are abundant and easily available. It is the result of pyrolysis treatment. The use of low-cost precursors such as biomass or waste residues has gained momentum in carbon research [7].
Polyvinylidene fluoride (PVDF), which consists of a CH$_2$-CF$_2$ is a highly non-reactive and pure thermoplastic fluoropolymer that can become ferroelectric. Thus, PVDF is the electro-active, semi-crystalline polymer with pyro and piezoelectric properties at room temperature, and oxidative resistances which has led to many applications [8].

The development of porous materials is very promising for use in applications, such as encapsulation of active substances as a support for catalysts and lightweight solvents [9], energy materials such as gas diffusion layer, which is component of proton exchange membrane fuel cell [10] and as energy storage materials such as hydrogen storage [11]. Thus, an improved method for making porous material is required, so that it is effective, simple, and cost saving in the manufacturing process. Liquid nitrogen cold quenching is a simple and controllable method to increase porous [12]. The quenching is also a method used to determine hardenability of electrical conductivity material [13].

In this study, we have investigated the porous, hardness, and electrical conductivity of C/C composite based on GEW from EAF waste, NCB from coconut fibers had been made through the pyrolysis and PVDF as the binder with used liquid nitrogen cold quenching treatment.

2. Experimental Methods
The main material GEW from the EAF was chosen as a reinforcement material for electrically conductive material due to its similarity with synthetic graphite. GEW powder (particle size < 44 μm) from iron or steel smelting factory was used as an additive. Structural examination of GEW from the EAF showed the crystalline carbon structure, instead of amorphous structure, which implies that it has good conductivity [14]. Meanwhile, NCB powder from coconut fiber (particle size of < 44 μm) was used as filler.

Preparation of carbon materials was done using following procedure. NCB powder was conducted in the carbonization process. Coconut coir was carbonized at temperature of 500°C for an hour in a furnace with nitrogen atmosphere. Subsequently, the charcoal was pyrolyzed at temperature of 1300 °C for an hour. Furthermore, commercial-grade PVDF powder (supplied by Sigma-ALDRICH Inc., USA 182702-2506) was used as binder. Material GEW/NCB/PVDF was made by mixing 70wt% GEW, 10 wt% NCB, and 20 wt% PVDF. Total weight composition to make raw material of

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Figure 1. Flow diagram of GEW/NCB/PVDF composites preparation using the liquid nitrogen cold quenching.
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conductive GEW/NCB/PVDF composite is 20 gram with non-solvent. The GEW/NCB/PVDF composite was mixed with a ball mill for 900 minutes, and molded using compression hot press machine at pressure of 5.5 MPa and temperature of 150°C for 60 minutes with sample dimension of $5 \times 5 \times 0.3$ cm$^3$. After that, GEW/NCB/PVDF composite was put into liquid nitrogen quickly for cold quenching (Figure 1). The whole experimental process is principally quite simple but it has high impact.

Electrical conductivity used in this measurement is The HIOKI 3522-50 LCR HiTESTER to measure the AC electrical conductance of the samples composite materials. SEM from HITACHI SU-3500 was used to observe the morphology of the surface of the samples. Physical tests of properties porosity and density were measured using ASTM C20.

3. Results and Discussion
In this experiment GEW/NCB/PVDF composite was made into a bulk C/C composite. After that, GEW/NCB/PVDF composite was put off into liquid nitrogen quickly. The GEW/NCB/PVDF composite sample is shown in Figure 2. The quenching is the process of suddenly cooling a material from high temperature. The quenching is also a method used to determine the hardenability of materials and increase porous.

![Figure 2. The GEW/NCB/PVDF composite sample.](image)

In Figure 3, the hardenability was shown for GEW/NCB/PVDF composites. GEW/NCB/ PVDF composite with liquid nitrogen cold quenching treatment has higher hardness value compared to GEW/NCB/PVDF composites without treatment. The increase in the value of hardness in the GEW/NCB/PVDF composite due to two major energetic contributions including the increase of the elastic energy and the decrease of the free energy. Therefore, the driving energy for the rolling of a bonding molecule between GEW, NCB, and PVDF must overcome the strain energy of the binding molecule. In our experiment, the hardness of the GEW/NCB/PVDF composite would occur when the GEW/NCB/PVDF composite is cooled quickly by liquid nitrogen, resulting in temperature difference of energetically favourable states. When the hot GEW/NCB/PVDF composite was put into the liquid nitrogen, the larger temperature difference is provided then resulting in better rolling a bonding molecule between GEW, NCB, and PVDF for GEW/NCB/PVDF composites. The use of liquid nitrogen cold quenching treatment increases hardness value of GEW/NCB/PVDF composites. Moreover, we believe that, once the rolling happened of a bonding GEW, NCB, and PVDF molecule, the van der Waals interaction of overlapping regions of the GEW/NCB/PVDF composite would increase its structural stability. In addition, the total surface energy of all GEW/NCB/PVDF composite could be minimized by tightly wrapping adjacent bonding molecule to scroll together. The use of PVDF obtains good mechanical properties and the quenching temperature also has a great influence on the mechanical properties of the resultant, which can be elucidated by its great effects on the GEW/NCB/PVDF composite morphologies.

In Figure 4 (a) and (b), GEW/NCB/PVDF composite morphologies were observed by SEM. In the GEW/NCB/PVDF composites using the liquid nitrogen cold quenching (Figure 4 (b)), there are many cracks in the initial GEW/NCB/PVDF composites due to the breakdown of the molecular bonding of
GEW, NCB, and PVDF which cannot be avoided during strong oxidation and peeling of PVDF powders. It can be explained by crystallization of PVDF. The crystallization process of crystalline PVDF consists of nucleation process and the crystal growth process.

![Figure 3](image-url)  
*Figure 3. The hardness of GEW/NCB/PVDF composite.*

![Figure 4](image-url)  
*Figure 4. SEM micrograph of GEW/NCB/PVDF composites (a) before and (b) after treatment using the liquid nitrogen cold quenching.*

The molecular chains had more time to arrange around the fewer nuclei at higher quenching temperature, with the decrease of the quenching temperature, cooling rate and driving force increase, so that more stable nuclei was formed. Thus, when liquid nitrogen was used on the GEW/NCB/PVDF composite, the sample was cooled quickly because the system needs deeper degree of supercooling to form stable crystal nuclei. When the GEW/NCB/PVDF composite was put into a liquid nitrogen bath driving the blend to undergo S–L phase separation, it obtains many formation of sponge-like pore structure compared to GEW/NCB/PVDF composites without treatment (Figure 4 (a)). In addition, there were nitrogen adsorption-desorption isotherm events and pore size distribution process that decreases density of GEW/NCB/PVDF composite. This can be seen from table 1 showing the percentage of porosity and density produced.

Table 1 also shows that the GEW/NCB/PVDF composite with liquid nitrogen cold quenching treatment has a higher electrical conductivity value than GEW/NCB/PVDF composites without treatment. Since the formation of many percolation junctions for electric current between GEW and NCB and PVDF crystallization which has weak electrical conductor properties.
Table 1. The parameters of GE GEW/NCB/PVDF composite.

| Material                                | Porosity (%) | Density (gr/cm$^3$) | Hardness (VHn) | Conductivity (S/m) |
|-----------------------------------------|--------------|---------------------|----------------|-------------------|
| GEW/NCB/PVDF untreated                 | 5.0          | 0.9                 | 4.0            | 280               |
| GEW/NCB/PVDF using liquid nitrogen cold quenching | 7.5          | 0.7                 | 6.0            | 430               |

4. Conclusions
We have observed the electrical properties of GEW of EAF and NCB of coconut fibre as C/C composite with PVDF as the binder and by process non-solvent to increase the value of conductivity. GEW/NCB/PVDF composite was processed using non-solvent technique to make bulk composite with size $5 \times 5 \times 0.3$ cm$^3$. Preparation of GEW/NCB/PVDF composite by using the liquid nitrogen cold quenching is a simple and controllable method to increase porous. The quenching is also a method used to determine hardenability of materials and electrical conductivity of GEW/NCB/PVDF composite. Increase in the value of hardness as much as 6 VHn in the GEW/NCB/PVDF composite due to dominant two major energetic contributions including the increase of the elastic energy and the decrease of the free energy. There are many cracks in the initial GEW/NCB/PVDF composites due to the breakdown of the molecular bonding of GEW, NCB and PVDF which cannot be avoided during strong oxidation and peeling of PVDF powders that form crystalline. Nitrogen adsorption-desorption isotherm events and pore size distributions affect to decreased density become 0.7 gr/cm$^3$ of GEW/NCB/PVDF composite. The high value of conductivity 430 S/m is obtained for the GEW/NCB/PVDF treated. It is concluded that the preparation of GEW/NCB/PVDF composite by using liquid nitrogen cold quenching could increase porous, increase the value of hardness, decrease density, and increase electrical conductivity material.

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