

Mechanical and Barrier Properties of PVP-Carbon Dot Nanocomposite Films

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Abstract

In this research, carbon dot was synthesized from citric acid and urea through a single step microwave process, and Poly Vinyl Pyrrolidone (PVP) films composited by carbon dot were prepared. The effects of different composition carbon dots on mechanical strength of films and water vapor barrier were evaluated. Highest mechanical yielded composite film were analyzed their thermal stability. Average of carbon dot diameter was found 90.61 nm and polydispersity indices 0.396. Different composition carbon dot exhibit significant improvement in tensile strength and modulus. Water permeability of films variate with the content of carbon dot. The presence of carbon dot had a negligible effect on Tg of film and show melting process.

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1. INTRODUCTION

Composite materials harness many polymer types develop into materials with extensive range field of application. Nano technology establish composite polymers with nano-sized fillers that produce enormous internal surfaces against volumes between nanoparticles and polymer matrix making them superior to traditional composites [1]. Nanocomposite improvement on mechanical property of polyvinyl alcohol [2], electrical properties of polyvinylidene fluoride [3], and photodegradation capability of polyvinyl chloride [4].

Carbon dots own unique advantages including low toxicity, simple preparation, chemical inertness, biocompatibility, easy functionalization, and new class photoluminescence. Application of carbon nano particle interest in many fields which driven robust production. The producing follows either top-down or bottom-up techniques. However, each technique has distinct advantages and disadvantages related to the uniformity of particle size, quantum yield, and conditions [5]. Among bottom-up techniques, microwave offers carbon nano particles preparation

efficiently in time and energy consumption compared with else such as hydrothermal oxidation [6].

Polyvinyl pyrrolidone (PVP) has a lot of application in pharmaceutical products, cosmetics [7], metallurgy, electronics, and polymers. Role of PVP contributed to synthesis nanoparticles are surface stabilizers, shape control, reducing agents and dispersants [8]. However, study composite films PVP with nano particles was found on optical improvement using Ce(SO₄)₂ [9] and Ag and Au [10].

This study synthesized composite film by incorporating carbon dots with <100 nm diameter at small amount into PVP and observed how a minute quantity of carbon dot affect significantly on PVP characteristics. Due to its nano scale size, it interacts with matter at the atomic, molecular, or macromolecular level. Characterization carbon dot on reinforcement, transport and thermal effect on the film were studied while spectroscopy methods followed photoluminescence property of carbon dot.

2. EXPERIMENTAL SECTION

2.1. Materials

Citric acid anhydrous (>99% purity, Merck), Urea (>99% purity, Merck) and PVP K90 (Pharmaceutical grade, Ashland).

2.2. Methods

2.2.1. Synthesis of carbon dot

A mixture of 1 gr citric acid and 1gr urea in 10 ml water was heated in a 300 W microwave oven for 4-5 minutes. Brown solution was centrifuged at 3000 rpm for 20 minutes and filtered using a Millipore 0.2 μm membrane. The final solution was dried by oven at 70°C for 24 hours to obtain a solid carbon dot for further experiment.

2.2.2. Particle size analysis

A mixture of 10 mg solid carbon dot in 10 ml of water was sonicated for 10 minutes. A sample of 3 ml of solution was poured into a single-use cuvette and measured on MALVERN Instrument Mastersizer 3000 particle analyzer.

2.2.3. Analysis of absorption spectrum

A mixture of 10 mg solid carbon dot in 10 ml of water was sonicated for 10 minutes. Sample of 3 ml was poured into cuvet and measured absorption at range 200 – 800 nm on UV-Vis Shimadzu Pharmaspec 1700.

2.2.4 Analysis of fluorescence spectrum

A mixture of 10 mg solid carbon dot in 10 ml of water was sonicated for 10 minutes. A sample of 3 ml was poured into cuvet and measured on FLUOstar Omega-BMG LABTECH fluorometer appliance with excitation wavelength 365 nm.

2.2.5 Preparation composite film

A mixture of carbon dot in 10 ml of water was sonicated for 10 minutes. Dissolved 3 g of PVP in the mixture and sonicated for 30 minutes to obtain viscous brown polymer

solution. PVP-carbon dot mixture was cast on a 25 cm x 25 cm glass plate and dried at temperature 20° C and 60% R_H for 24 hours. Compositions of carbon dot were 0.1% w/w, 0.3% w/w, 0.5% w/w, 0.7% w/w, 0.9% w/w, 1% w/w and 0.0% w/w as a controls.

2.2.6 Tensile strength analysis (ASTM D638 2005)

Tensile strength and percentage elongation were measured using INSTRON 3369 tensile machine at crosshead speed 25 cm/min [11]. Test specimen width 20 mm, length 120 mm and range thickness 0.07-0.1 mm.

2.2.7 Water vapor permeability analysis (ASTM E 96-95)

Specimen film with 10% surface area was glued on aluminum foil hole and placed on a test dish filled with water [12]. The dish was weighed and then put into oven at $[37 \pm 0.5]^\circ\text{C}$ and weighed change measured every 0.5 hours for 4.5 hours times. WVTR and WVP calculate using equation (1) and equation (2):

$$WVTR = \frac{\text{loss water weight}}{\text{time} \times \text{area}} \quad (1)$$

$$WVP = \frac{WVTR}{S \times \Delta R_H} \times d \quad (2)$$

WVTR: water vapor transmission rate ($\text{g s}^{-1}\text{m}^{-2}$)

WVP : water vapor permeability ($\text{g s}^{-1}\text{m}^{-2}\text{Pa}^{-1}$)

ΔR_H : relative humidity gradient

S : Saturated air pressure at 37°C

d : thickness (m)

2.2.8 Thermal analysis

A film of 10 mg was put on in an aluminum cup then placed on a furnace of Shimadzu DSC 60. The instrument was heated in the range 30-200°C with rate $10^\circ\text{C min}^{-1}$.

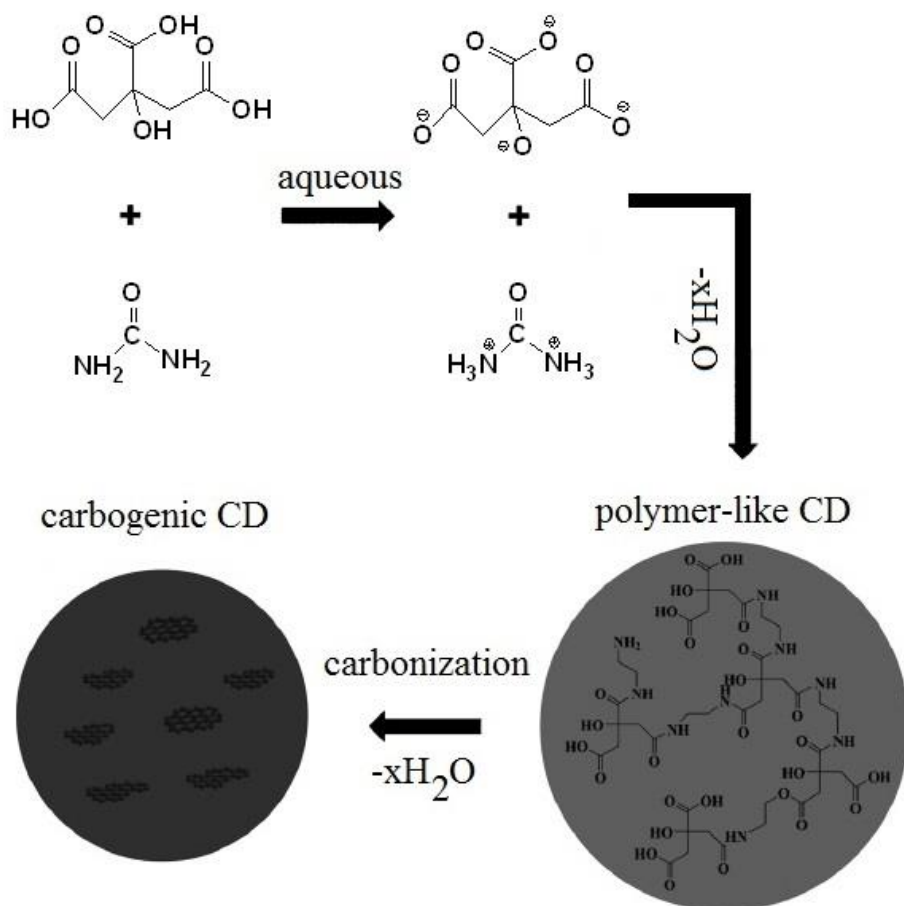


Fig. 1. Synthesis reaction citric acid – urea carbon dot

3. RESULT AND DISCUSSION

3.1. Synthesis of carbon dot

The reaction between citric acid and urea using a microwave oven produced a carbon dot solution. After followed washing, separation and drying process then solids carbon dot was obtained with rendement 40%. Formation process carbon dot-based citric acid involving condensation, polymerization, and carbonization (Fig.1). The carbon dot powder was highly hygroscopic caused by urea as nitrogen-doping and long-term storage in ambient atmosphere resulted in the powders that stuck to the inner walls of the vials.[13].

3.2. Absorption and Emission Spectrum of Carbon Dot

Absorption and emission spectrum of the carbon dot solution were shown in figure 2. The absorption spectrum of a peak is shown at 340 nm which characteristic transition $n-\pi^*$ of $C=O$ group on carbon dot surface. This typical transition reported on carbon dot synthesized from citric acid and ethylenediamine [14]. Nanoparticles in solution change the optical property that is sensitive to the size, shape, agglomeration and particle concentration [15]. Therefore, absorption peak in ultraviolet region proves carbon dot nanoparticles present.

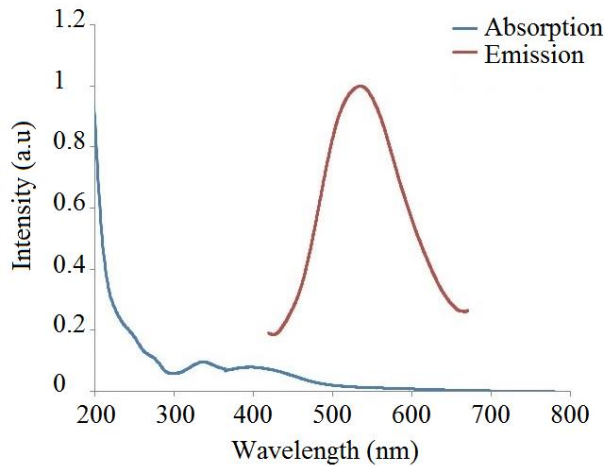


Fig. 2. Normalized spectrum absorption and emission of carbon dot solution

The emission spectrum of fluorescence in Figure 2 shown a maximum peak at 535 nm in a visible region. Characteristics of the fluorescent emission spectrum width to the carbon dot are the result of the superposition of the combined response of the individual emitter in the form of fluorophore and functional groups on the surface of the carbon dot. While optical observation upon carbon dot solution with irradiation at 366 nm formed a green color solution.

3.3. Particle Size of Carbon Dot

Particle size measurement of carbon dot was provided average particle diameter 90.61 nm and polydispersity index (PI) of 0.396 (Fig. 3). The average carbon dot particles less than 100 nm categorized as a nano particle. However, this result was achieved after additional separation by filtration and diminished broadly distributions carbon sizes generated in microwave synthesis procedures. This method simplified separation procedure instead of utilizing high ultracentrifugation and dialysis to acquire homogeneous particle size distribution [16].

While PI value lower than 0.5 where it was a threshold of narrow particle size distribution requirement and the carbon dot distribution was not monodispersed. In addition, PI values also informed inclination for particles agglomeration on short storage time

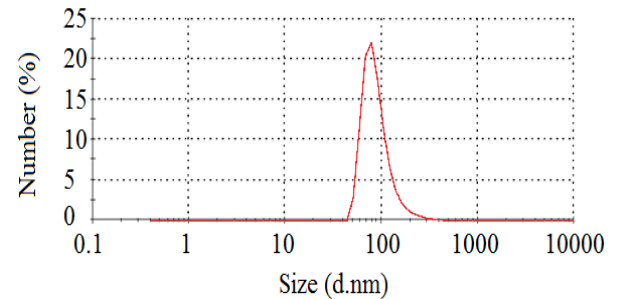


Fig. 3. Particle size distribution of carbon dot

Otherwise, the result showed less probability agglomeration occurred which it prolong storage time solution of the carbon dot.

3.4. Tensile Test Film PVP - Carbon Dot Nanocomposite

The tensile strength result of the composite film increased within the range of carbon dot content (Fig. 4). Maximum tensile strength at 0.7% w/w carbon dot had 60% higher, and elongation 8.6% than control and the modulus Young had 0.57 Mpa. While film with 1% w/w show declining tensile strength caused by increasing carbon dot undergo agglomeration reducing internal surface area. The elongation result showed the highest value 14.8% at 1% w/w carbon dot film that increased carbon dot quantity could induce slip zone more than hindrance effect.

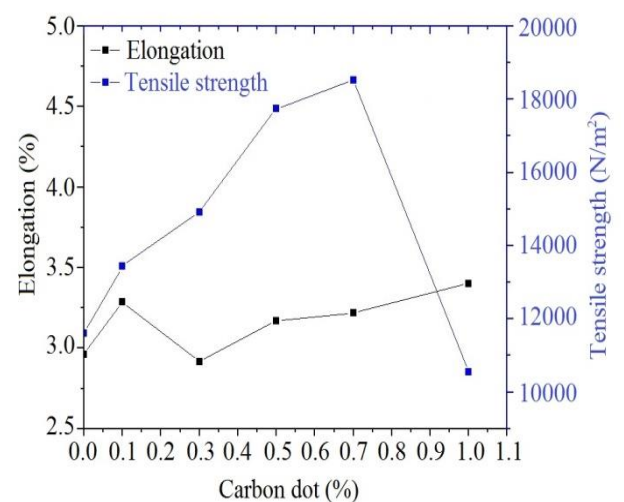


Fig. 4. Effect of carbon dot on composite film tensile strength and elongation

Consider PVP composite film with carbon dot average size of 90.61 nm and at low

concentration agree with criteria of nanocomposite cause by significant changes in mechanical property [17]. Low-percolation threshold, correlation of orientation and inter-particle positions arising at small volume fractions theoretically rationalized nanocomposite nature.

3.5 Water Vapour Permeability of Film PVP-Carbon Dot Composite

Water vapor transmission rate and permeability through hydrophilic films depend on diffusivity and solubility of water molecules. The results of the water vapor transmission rate of the composite films were decreasing exponential against time (Fig. 5). High water

affinity of the polymer quickly draws water vapor into the film. While the carbon dot content influenced the transmission rate at initial measurement.

Water vapor permeability result of the films was shown in Fig 6. The carbon dot content changed water permeability of the composite films and maximum value found at 0.7% carbon dot. Compared with control, the increasing carbon dot content accelerated water permeability of the films. However, retardation water permeability at 0.9% w/w occurred as hindrance effect and path length caused by growing size agglomeration carbon dot. It also found on film composite of protein isolate and carbon dot where retardation water permeability occur at higher concentration [18].

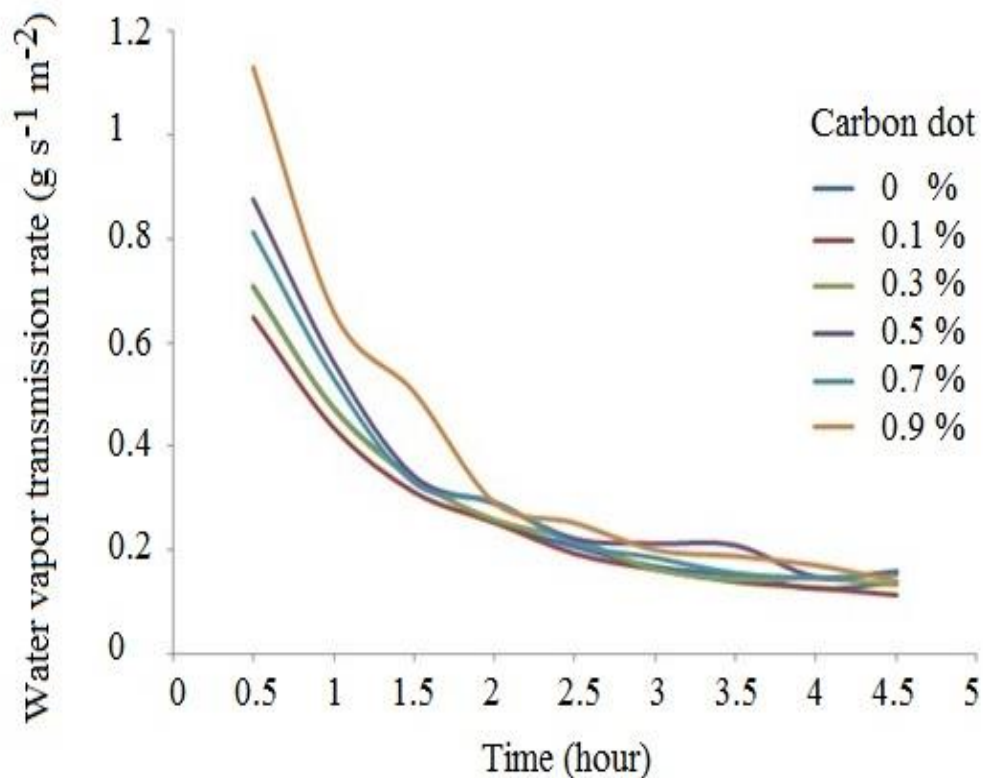


Fig. 5. Water vapor transmission rate vs. time

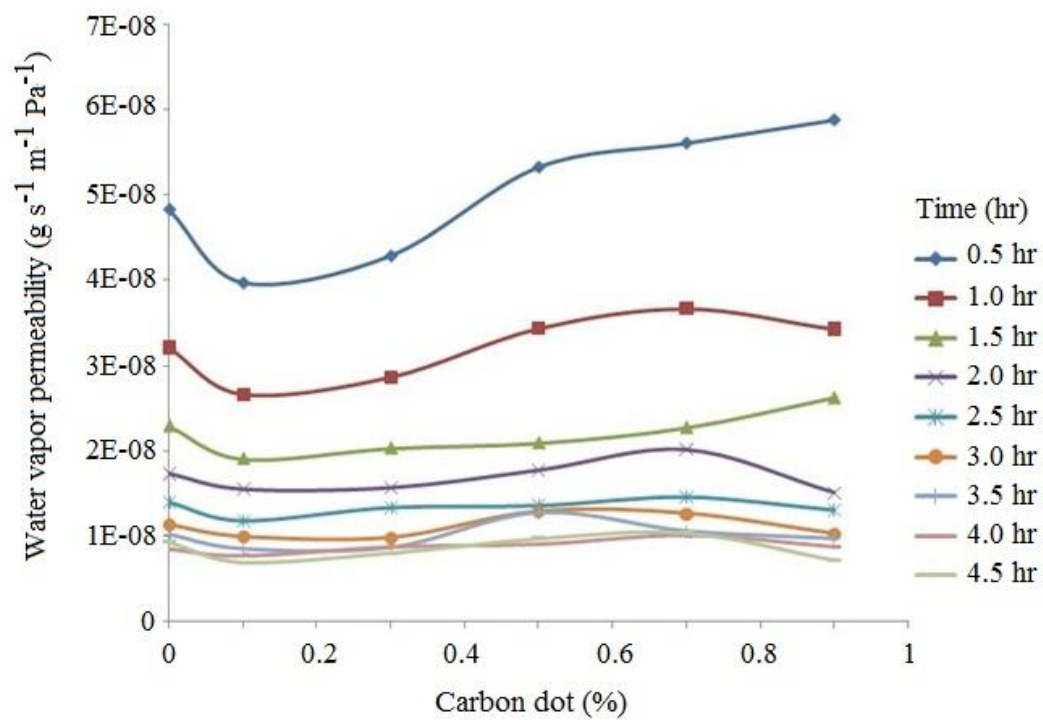


Fig. 6. Water vapor permeability vs. carbon dot (%)

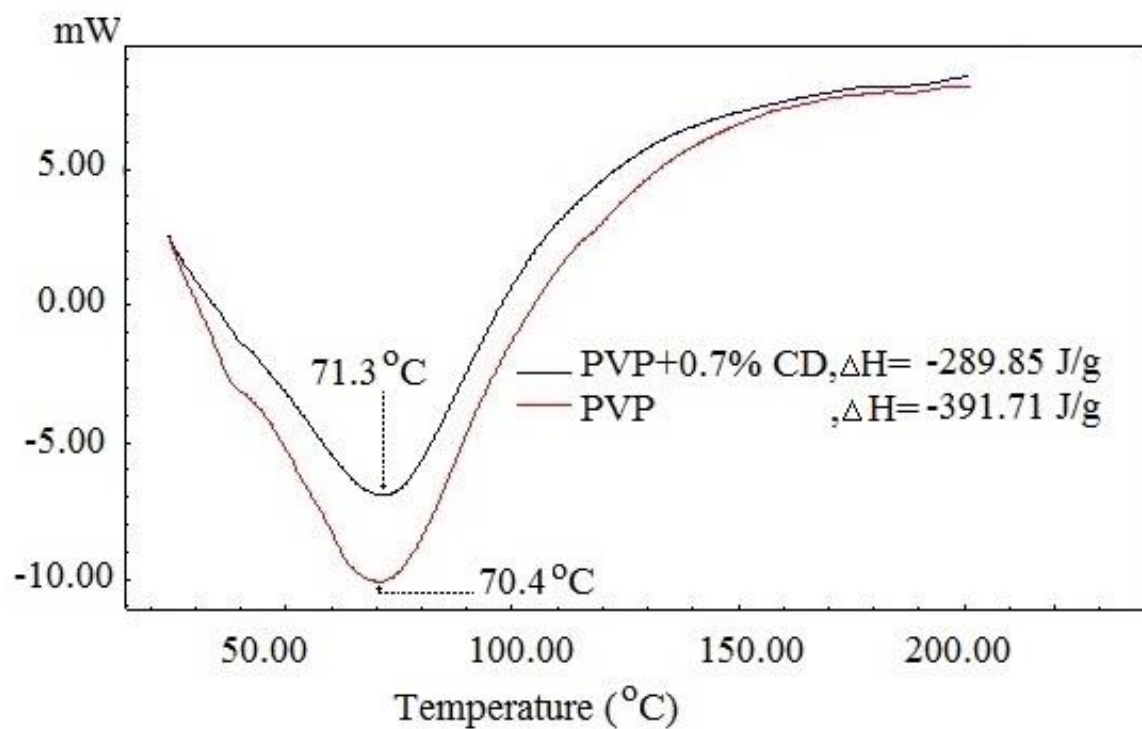


Fig. 7. Thermogram of films PVP+0,7% w/w carbon dot and PVP

3.6. Thermal Property of Film PVP-Carbon Dot Composite

Thermal measurements of PVP film and PVP nanocomposite contained 0.7% w/w carbon dot film brought up an asymmetric melting peak (Fig. 7) caused by heat for releasing water on polymer matrix that different in peak magnitude indicating carbon dot on film already substitute water. Glass temperature (T_g) at 177 ° C in powder form, while it was not found on film form as casting process influenced inter-polymers chain arrangement. This observation agrees with El-Kader and Abdeen [19] report on T_g peak of PVP 40000 molecular weight. Peak maxima of PVP with 0.7% w/w carbon dot slightly higher than PVP film show a thermal resistance contribution of carbon dot.

4. CONCLUSION

Successful carbon dot was synthesized based on citric acid and urea using single step microwaves. The carbon dot has shown photoluminesces property. The average particle diameter of the carbon dot was 90.61 nm and polydispersity indices 0.396.

The tensile strength of modified films increases significantly with the addition of carbon dot 0.1% w/w - 0.7% w/w and is categorized as a nanocomposite. The film composition with 0,7% w/w carbon dot has increased mechanical strength by 60% and elongation by 8.6% than control. The transmission rate of water vapor show combination water affinity of PVP and hygroscopic carbon dot accelerated water vapor transport. Water permeability retardation occurred at higher carbon dot content.

Thermograms of modified and unmodified film show an endothermic peak for releasing binding water and related homogeneous phase of the films. Carbon dot content had a negligible influence on changing T_g of PVP.

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