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Review Article

Transparent Conductive Far-Infrared Radiative Film based on Polyvinyl Alcohol (PVA) with Carbon Fiber (CF) in Agriculture Greenhouse

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Abstract

There are many types of transparent conductive films, the most common being made by depositing ITO (indium-Tin-oxide) on ultra-thin glass substrate by physical or chemical methods. In this study, PVA was used as basis material and CF as electrical conductive material, to mix both two materials and distribute the CF in the PVA solution, then by casting form transmittance electrical conductivity film. The newly developed film has an average Edge-to-Edge Resistance of 2069.58 Ω, light transmittance of 75.75% and has a heating capability of 23.38 W/m^2 via far-infrared light (sample size is 200*200 mm and voltage in 220 V, through setting the facts, the Block Resistance reach 419.9208 Ω, heating capability of 115.26 W/m^2 via far-infrared light, and the Light Transmittance reach 58.2790%,). The film is almost clearly transparent and is suitable for deployment as part of the retaining structure of agricultural greenhouses as it allows adequate sunlight penetration for the necessary photosynthesis of crops. This film is promising for the "solar greenhouse" industry and able to solve the long-term problems of agriculture in seasonable regions such as northern China during the winter. This film is a suitable energy efficient replacement to the current greenhouse facilities conventional electrical heaters to meet the temperature needs of crop growth.

Keywords: *Transparent conductive film, Conductive film, Transparent film, PVA, Carbon fiber*

Introduction

In recent years, researchers have developed a series of new transparent conductive films that can replace ITO, such as conductive polymers, carbon nanotubes, graphene and metal nanostructures [1]. The paper "Transparent Conductive Far-Infrared Radiative Film based on Cotton Pulp with Carbon Fiber in Agriculture Greenhouse" descried have developed a transparent conductive film by depositing conductive carbon fiber on cotton pulp substrate. The newly developed film has an average Edge-to-Edge Resistance of 545.65 Ω, light transmittance of 67.9% and has a heating capability of 88.70 W/m2 via far-infrared light. The film is almost clearly transparent and is suitable for deployment as part of the retaining structure of agricultural greenhouses as it allows adequate sunlight penetration for the necessary photosynthesis of crops. This film is promising for the "solar greenhouse" industry and is able to solve the long-term problems of agriculture in seasonable regions such as northern China during the winter. This film is a suitable energy efficient replacement to the current greenhouse facilities conventional electrical heaters to meet the temperature needs of crop growth [2].

This study research and develop a flexible transparent far-infrared radiation film made with CF as conductive material and PVA matrix respectively. The film is a kind of transparent conductive film, by flexible can be used as the retaining structure of agricultural greenhouses, by transparency can make the sun shining through, meet the needs of crop photosynthesis, by conductivity can make its radiate far infrared light, crop growth is the light of life, can meet the needs of agricultural greenhouse warming. The cheap raw materials and simple manufacturing process are suitable for the realization of industrial mass production, and can be used in the application of greenhouse heating and light supplement in facility agriculture, which is also the vitality of this study.

At present, the most widely used transparent conductive films are prepared on hard substrates such as glass and ceramics. Compared with the rigid transparent conductive film, the transparent conductive film prepared on the organic flexible substrate not only has the same photoelectric characteristics, but also has many unique advantages, such as: flexible, light weight, not easily broken, can be used to improve the efficiency of the industrial continuous production mode, easy to transport, etc. With the development of electronic devices towards lightening, flexible transparent conductive film is expected to become a replacement of rigid transparent conductive film.

From the perspective of the development pattern of modern facilities and horticulture in the world, most modern greenhouses which plastic film greenhouses are about 600,000 square kilometers, mainly distributed in Asia. Glass greenhouse about 40,000 square kilometers, mainly distributed in Europe and the United States. New cover material polycarbonate board (PC board) greenhouse in recent years, the development speed is very fast, at present about more than 10 thousand hectares, sporadic distribution in the world.

One important area, to apply flexible transparent conductive film, is the Protected Agriculture, the greenhouse, as a modern precision agriculture facility, has realized the artificial control of temperature, light, water, gas and fertilizer in the greenhouse to form an environment conducive to the growth of crops. In developed countries such as the United States and Israel, an intensive greenhouse industry has been formed. The greenhouse is a building with lighting covering material as the whole or part of the envelope structure material, which can be used for cultivating plants in winter or other seasons that are not suitable for the growth of open plants.

Greenhouse is a day lighting building, so light transmittance is one of the most basic indexes to evaluate the light transmittance of greenhouse. Transmittance is the percentage of the amount of light penetrating the greenhouse to the amount of light outside. The light transmittance of greenhouse is affected by the light transmittance of greenhouse cover material and the shadow rate of greenhouse skeleton, and the light transmittance of greenhouse is also changing with the different solar radiation Angle in different seasons. The light transmittance of greenhouse becomes the direct influence factor of crop growth and crop variety selection. In general, plastic greenhouse in 50%~60%, glass greenhouse transmittance in 60%~70%, solar greenhouse can reach more than 70% [3].

The transparent conductive film with both light transmittance and electrical conductivity makes it possible to integrate the enclosure structure and heating facilities of the agricultural greenhouse. According to the practical application experience of this kind of conductive film used for indoor heating, the resistance value of 900*600 mm conductive film is 96.8 Ω, the input power is 500 W (Voltage=220 V), and the surface temperature can reach 70~90°C. When the transparent conductive film in this experiment is used for heating in agricultural greenhouse, in order to avoid crops being roasted, the experience in the application process is that it is more appropriate to control the input power of the transparent conductive film at 200 W/m^2 (Voltage=220 V) and the surface temperature of the film can reach 30°C.

In order to make the vegetables grow normally in the cold winter, maintain the high yield, the greenhouse ceiling is applied in modern agricultural planting, through the adoption of the transparent material, forming the local small climate, and creating the environment that is suitable for the growth of the crop. However, it is not necessarily possible to achieve the temperature of the vegetables, so the average greenhouse ceiling will install the heating equipment to ensure that the temperature in the shed can make the vegetables harvest.

As a transparent infrared radiation material, the transparent conductive film can be used for the maintenance of structural materials in agricultural greenhouses. On the one hand, it can store heat energy through sunlight, on the other hand, it can radiate far infrared through electric excitation to compensate the temperature of crops. The actual measurement of the internal light illumination of the agricultural greenhouse, target of LT > 70% is good. (According to the measurement of the agricultural greenhouses in use now, the actual light transmittance in the greenhouses is generally 70% in sunny weather.)

Plastic film has the property of heat preservation. After covering the film, the turbidity in the greenhouse will increase with the increase of the outside temperature and decrease with the decrease of the outside temperature. There are obvious seasonal changes and large diurnal temperature difference. The lower the temperature period, the greater the temperature difference. Generally, the daily temperature increase in the greenhouse in cold season can reach 3-6°C, and the temperature increase ability on cloudy days or at night is only 1-2°C. In the warm spring season, the temperature difference between the shed and the open field gradually increases, and the temperature increase can reach 6-15°C. When the outside temperature rises, the temperature inside the greenhouse increases relatively, up to more than 20°C. Therefore, there are high temperature and freezing hazards in the greenhouse, which need to be adjusted manually. In high temperature season, high temperature above 50°C can be produced in the shed. The whole shed is ventilated, and the shed is covered with straw curtain or built into "awning", which is 1-2°C lower than the open air temperature. In winter, when the sun is clear, the minimum temperature at night is 1-3°C higher than the open field, and several branches are the same as the open field on cloudy days. Therefore, the main production season of greenhouses is spring, summer and autumn. Through heat preservation and ventilation and cooling, the temperature of the shed can be maintained at 15-30°C for growth [4].

In winter, the commonly used agricultural greenhouse warming measures are:

1. One is to add a few warm fans in the shed, temporarily heating the place where the temperature is relatively low, but the need to pay attention to the high humidity in the shed, to avoid leakage caused by bad things.
2. The second it is if the greenhouse is adjacent to have the condition that can use, if the supply hot gas such as brewery, bathhouse can try to be used abounding, saved cost already the repeat use that completed resource.
3. The third is to cover the grass felt on the greenhouse, which is a relatively backward insulation method. What we need to pay attention to is to ventilate and receive abundant sunlight on time every day.

Plastic products have brought great convenience to people's life, but discarded plastic garbage has caused unimaginable harm to the ecological environment. Plastic waste that is difficult to degrade causes the death of hundreds of thousands of Marine animals every year, and the generated micro-plastics are all over the earth, and even enter the bodies of animals and plants or other environments, posing a great threat to human health. In order to better prevent and control plastic pollution, it is urgent to develop a new generation of sustainable plastic alternative materials. PVA film in the natural environment can be degraded by microorganisms and non-toxic, its degradation products for carbon dioxide and water, is a new generation of environmentally friendly plastic film material, it completely solved the white pollution caused by plastic film material [5].

With the deepening of people's environmental protection concept, the green packaging is getting higher and higher in the packaging field, and its varieties are also detected in endlessly. Water-soluble packaging film as an important type of green packaging materials, its good water solubility, barrier and environmental protection characteristics, more and more countries pay attention to the packaging field. Plants cannot grow everywhere. Their environment has to provide the right conditions for them to survive. Specifically, plants need water, air, sunlight, and suitable temperatures. In winter months, cold temperatures are often a limiting factor for plant growth [6]. Greenhouse heating is one of the most energy-consuming operational requirements during winter periods, having a significant impact on production cost [7]. The concept of heating greenhouses was first recorded in Korea in the 1400's, as people in that cold country realized that they could add to the sun's heat and open up more growing possibilities. Throughout the centuries the understanding of winter greenhouse technology improved, and farmers were able to precisely control the temperature, humidity, and chemical composition of the greenhouse atmosphere. Greenhouse heating systems eventually became automated, with digital controls and carefully regulated air circulation, and today's global agricultural industry relies heavily on them [8]. Elizabeth Waddington et al, in '7 Innovative Ways To Heat Your Greenhouse In Winter' said: As colder weather approaches, you're probably wondering whether your greenhouse is up to the task. Will it fend off the frosts well enough to keep your crops growing all winter long? Whatever type of greenhouse you have, whether glass or plastic, you may need to think about heating it if you live in a colder climate zone. Where winter temperatures regularly drop well below freezing, some heating might be necessary to enable you to grow food year-round [9].

Greenhouse production in winter consumes a lot of energy. It has been pointed out that the ratio of fuel consumption produced by greenhouse to dry matter produced by greenhouse vegetables is 5:1 or 10:1, a lot of energy consumption, only 40% to 50% percent utilization. In Japan, it takes 5 L of oil to produce l0 kg of cucumbers, 50% to 60% times more energy than grain production. In the world agricultural production in a year, 35 percent of the energy consumption for greenhouse warming, greenhouse energy consumption costs accounted for 15% to 40% percent of the total greenhouse production costs [10].

PVA is a water-soluble polymer, characterized by good compactness, high crystallinity, strong adhesion, made of film flexible and smooth, oil resistance, solvent resistance, wear resistance, good gas permeability, and special treatment with water resistance, a wide range of uses. PVA is non-toxic, tasteless and harmless to human body. It has a good affinity with the natural environment. It does not accumulate and is pollution-free. PVA film is a kind of green and environment-friendly functional material with PVA as the main body and additives such as modifier, which can be completely degraded by microorganism in soil after special processing. It can degrade into carbon dioxide and water in a short time, and has the effect of improving the land. The biggest advantage of polyvinyl alcohol film is water solubility, the biggest disadvantage is poor water resistance. The reason for the poor water resistance is due to the hydrophilic hydroxyl group (-OH) in its molecules. The water resistance of PVA films can be improved if the hydroxyl group can be properly closed and connected with water resistant groups. PVA contains hydroxyl groups, which can take place in all typical reactions of polyols. Choosing appropriate polycondensation compounds, in the case of a small amount of addition, can appropriately interact with the hydroxyl groups in PVA, so that PVA forms a strong three-dimensional structure, which stabilizes the air tightness of PVA under wet conditions and improves the water resistance [11].

In this study, functional materials (CF) were added into the PVA membrane to improve the function and status of the PVA membrane, so that it has infrared radiation function, anti-static function, and electromagnetic shielding function, enrich the application field of the PVA membrane, and make the PVA membrane get a new life. In the industry, PVA films are generally manufactured with the use of a casting machine with roller press. For cost effectiveness, this study adapts the wet method is adapted for preparing the film. First, CF filament is mixed in diluted PVA and glycerin solution, then slowly blended for up to 2.5 hours to ensure the CF filament is dispersed evenly, and then casted in a mold and left for air drying up to 48 hours in ambient room temperate. The resulting product is a thin and flexible PVA-CF transparent conductive film. The process consists of manufacturing the transparent conductive film based on PVA-CF, and install current-carrying then install insulating film on double - sided for PVA-CF.

Agricultural greenhouses are mainly located in rural areas and suburbs, where electricity and other energy are in short supply. It is difficult for traditional power grids to reach these areas [12]. Therefore, self-made aluminum air battery is used as power supply in this study. The chemical reaction of al-air cells is similar to that of zinc-air cells. Al-air cells use high-purity Al (99.99% aluminum) as the negative electrode, oxygen as the positive electrode, and potassium hydroxide (KOH) or sodium hydroxide (NaOH) aqueous solution as the electrolyte. Aluminum absorbs oxygen from the air and is converted to aluminum oxide in a chemical reaction when the battery is discharged. The development of aluminum-air battery is very rapid, and its application in EV has achieved good results. It is a promising air battery [13]. The Schematic diagram of aluminum air battery see Figure 1.

In agricultural greenhouse use, especially need to consider the requirements of environmental friendliness. In this study, K_2SO_4 is used as electrolyte (K_2SO_4 is a kind of high quality and efficient potassium fertilizer without chlorine). Aluminum-air batteries with K_2SO_4 electrolyte have a lower energy density than aluminum-air batteries with KOH or NaOH electrolyte, but they are environmentally friendly and can achieve long battery life. If the electrode material is directly immersed in the electrolyte structure (see the Figure 15, It has been running under load for 5 weeks), it can achieve 3 months of endurance, to meet the needs of a heating season.

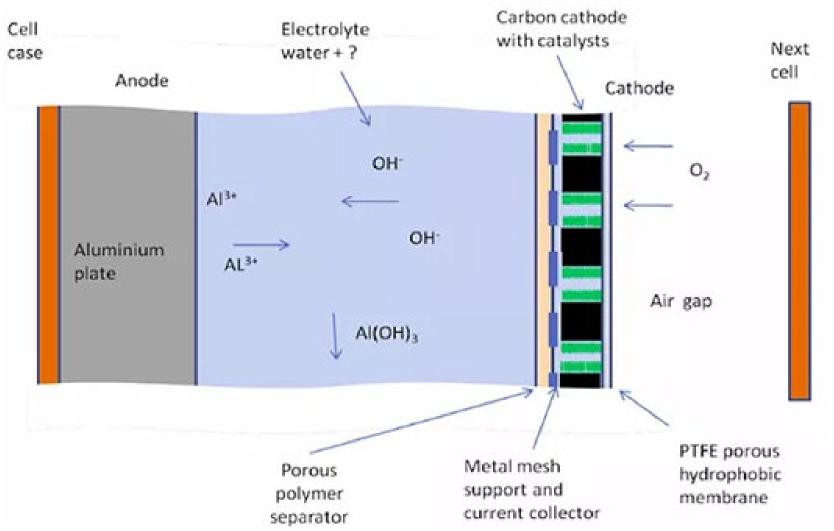

Figure 1: Schematic diagram of aluminum air battery.

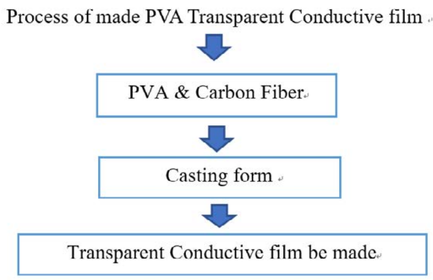

Figure 2: PVA transparent conductive film manufacturing process.

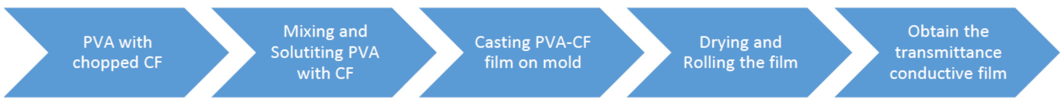

Figure 3: the process of fabricate polyvinyl alcohol with carbon fiber transmittance conductive film.

Results and Discussion

The wet method process of fabricating the PVA-CF film are as follows (see Figure 2). CF filaments are mixed with diluted PVA. The mixture is after two steps of casting coating and drying (heat treatment), PVA film products can be obtained by stripping and coiling. The process is very simple and easy to operate, which is an efficient production mode. As below Figure 3 extrusion blown film process: obtain PVA raw materials, water, plasticizer and lubricant (pigment) and other materials need to be prepared, and then through the forced cycle mixing, the next step is the process of extrusion granulation, the following steps are melt extrusion blown film, modified treatment, coiling and obtain the finished product. This process is more complex than the previous method, and is much less operational and productive [14].

Industrial fabricating transmittance conductive film for PVA-CF, general using dissolute machine system to dissolute the PVA, using filtering machine system to filter out impurities in PVA solution, using dispersing system to disperse CF in PVA solution, and using Casting machine system to casting form PVA-CF film, this process shows as Figure 4.

Experiments are conducted using PVA as substrate material infused with CF filaments of lengths 3 mm, 6 mm, and 10 mm. The CF filaments provides conductive properties to the PVA solution mix, and when casted it results in a transmittance conductive film. An initial experiment for testing the suitable length of the CF used. Table 1 shows the ratio of the components used in the fabrication of the various film samples. The samples were fabricated with CF filament of 3 mm, 6 mm and 10 mm length were respectively cut and stir mixed with 30 g of PVA and 400 ml of water for two hours. The samples, which are shown in Figure 6 can then be examined for the dispersion uniformity of the CF in the PVA solution.

The experimental results are shown in Figures 5 and 6.

Figure 5a shows the casting mold used for the test fabrication. From Figure 5b and 5c, it is observed that 3 mm CF filaments disperses well in the PVA, while the distribution of the 6 mm filaments is very uneven, and lumpy agglomerations have formed throughout the casted film. Meanwhile, Figure 5d shows that the 10 mm filaments are hardly dispersed in PVA solution and the fibers are entangled into groups, which is expected to interfere with the process of forming thin conductive films.

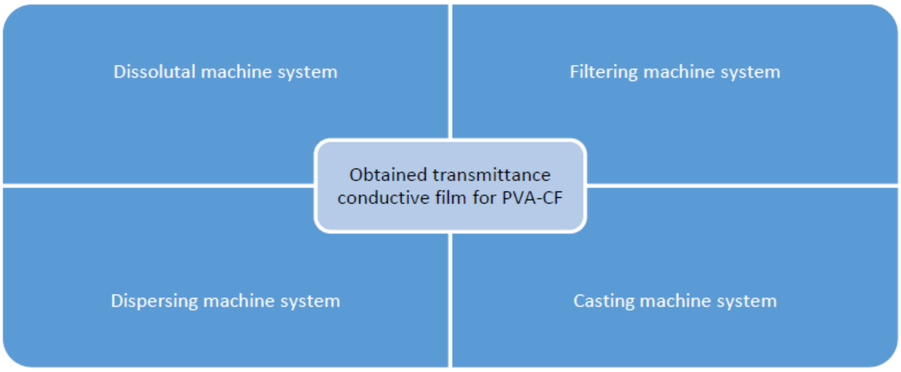

Figure 4: Four System industrial fabricating transmittance conductive for PVA-CF.

Figure 5: Different length carbon fiber dispersing in PVA solution (a) 3 mm, (b) 6 mm, (c) 10 mm.

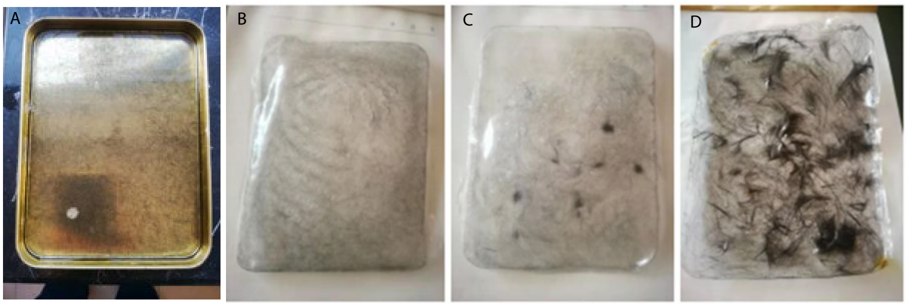

Figure 6: Casted film with carbon fiber in PVA solution: (a) Casting mold. (b) Film with 3mm CF filament. (b) Film with 6mm CF filament. (d) Film with 10mm CF filament.

Table 1: Mixture ratio for fabrication of films with carbon fiber of various lengths.

Materials	CF-3 mm	CF-6 mm	CF-10 mm
CF (g):PVA (g)	0.3:30	0.3:30	0.3:30
Glycerin (mL)/(g)	15/18.95	15/18.95	15/18.95
H_2O (mL)	385	385	385

Glycerin concentration is 1.26362 g/mL. Stir mixing time is 2 hours.

As the films are applied to agricultural greenhouse as heating films with high light transmissivity, the film needs to be thin with uniform conductivity. Overall, the experiment result shows that the carbon fiber filaments of lengths 6 mm and 10 mm do no disperse uniformly in the PVA solution and are not suitable for fabrication of thin transmittance film with uniform conductivity. In conclusion, the optimum CF length for film fabrication is 3 mm as it allows for the good dispersion of the CF in the PVA solution. Thus all other experiments were conducted using only 3 mm carbon fiber filaments. Table 2 shows the results of the 12 samples of pure PVA films and PVA-CF films tested for light transmissivity. It is noted that PVA film is superior to other films in glossiness and transparency, and when compared to common cellophane (PT) and PVC film, PVA film has reflectivity property and light transmissivity that is higher by 20% and 50% respectively.

Table 2: Properties of fabricated Pure-PVA with PVA-CF film.

No.	Pure-PVA	CF-PVA	
	LT (%)	LT (%)	Edge-to-Edge Resistance (EER, Ω)
01	91.02	77.80	3140
02	87.33	74.92	2140
03	89.76	75.15	2220
04	89.12	80.18	1750
05	88.83	74.92	2140
06	90.60	78.49	1410
07	90.73	76.63	1950
08	88.43	79.87	3170
09	90.73	69.13	1340
10	90.57	75.66	1840
11	90.30	72.94	1900
12	88.73	71.30	2730
Mean	89.68	75.75	2069.58

Sample size is 200 mm x 200 mm. Carbon fiber filament length is 3 mm, carbon fiber to PVA ratio is 1:100. LT denotes light transmissivity while EER denotes edge-to-edge resistance. Pure PVA film is nonconductive and has infinite edge to edge resistance. A sample calculation of using 220 V and Block Resistance of 419.9208 Ω gives heating capability of 115.26 W/m2 via far-infrared light.

In agricultural greenhouses, transmittance of sun light is essential for crop growth. Light transmissivity reflects the percentage of direct sun light from the environment that is passed through the greenhouse walls to the interior. As this percentage is affected by the incident angle of the solar radiation in different seasons, the necessary light transmissivity needed for various crops differs, and materials used for the outer structure of agricultural greenhouses vary depending on the crops. In general, the light transmissivity of plastic greenhouse is 50%~60%, whereas that of glass greenhouses is 60%~70% and solar greenhouse typically achieve a light transmissivity of more than 70% (Table 2).

When compared to pure PVA films (which have an average light transmissivity of 89.68%), the PVA-CF films (which have an average light transmissivity of 75.75%) have 15.53% lower light transmissivity. This is mainly due to the added CF blocking the light transmitted through the film. This value indicated that the film is suitable for solar greenhouses. For application of the film in agricultural greenhouses in regions with seasonal weather, electrical energy is also needed to be delivered to the film for heating purposes. The addition of carbon fiber filaments to PVA films makes the PVA-CF film electrically conductive. Table 2 shows that the average EER measured is 2,069.58 Ω, which is suitable for the conversion of electrical energy to heat. A discussion of the generated heat will be presented as a later section. Table 4 in Supporting Information shows the effects of various CF to PVA ratio on the Edge-to-Edge Resistance (Ω) or Block Resistance (Ω) and light transmissivity (%) properties of the PVA-CF film. The films are fabricated in sets of 5 different carbon fiber to PVA ratios: 0.1:30 (0.33%), 0.2:30 (0.66%), 0.3:30 (1.0%), 0.6:30 (2.0%) and 1.0:30 (3.33%) (which translates to carbon fiber percentage of 0.33%, 0.66%, 2.0%, and 3.3% respectively). The effect of solution volume on the achievable thickness of the final molded film is also presented in the table.

From the first set of results in Table 4, it is observed that a low carbon fiber to PVA ratio of 0.1:30 (0.33%) produces film samples with average edge-to-edge resistance of 554.5 kΩ and average achievable light transmissivity of 75.825%. While the light transmissivity is optimum, the low range of conductivity is not suitable for infrared application in the agricultural greenhouse settings.

When the samples are fabricated using high carbon fiber to PVA ratio of 1:30 (3.33%), the extreme opposite effects are observed. The edge-to-edge resistance average value is 280.85 Ω and average achievable light transmissivity is only 36.89%. While the resistance is suitable for infrared application, the light transmissivity is too low. In general, for infrared applications, an edge-to-edge resistance below 1 kΩ is suitable, while for agricultural greenhouse applications, a light transmissivity value of approximately 60% is comparable to plastic and glass greenhouses. For the results shown in Table 4, is can be seen that film samples with carbon fiber to PVA ratios of 0.2:30 (0.66%), 0.3:30 (1.0%) and 0.6:30 (2.0%) have edge-to-edge resistances suitable for infrared applications.

Figure 7 shows the effects of film thickness on the block resistance, which directly affects the usability of the film in infrared applications. As shown in Figure 8, block resistance decreases with increased thickness. While this indicates that thicker films have good electrical properties for infrared applications, it also translates to an inverse effect of poor light transmissivity as previously discussed. Thus, a balance between the two inversely related properties needs to be made when deciding on film thickness.

From the various graphs shown in Figure 7, it is observed that samples with a CF:PVA ratio of higher than 0.3:30 (1.0%) have suitable edge-to-edge resistances across all film thickness range, while samples with a CF:PVA ratio of 0.2:30 (0.66%) and above are only suitable when thickness is greater than 7.5 mm, and samples with a CF:PVA ration of 1:30 (0.33%) have extremely high edge-to-edge resistances and are not suitable across all film thickness range. Figure 8 shows the relationship between light transmissivity vs. film thickness, which directly affects the suitability of the film as building material for agricultural greenhouses. As shown in Figure 8, light transmissivity reduces with increase in film thickness. In other words, the transmittance of the film is inversely proportional to the thickness of the film. To achieve suitable light transmissivity, thinner films are necessary.

The various graphs in Figure 8 shows that samples with a CF:PVA ratio of lower than 0.3:30 (1.0%) have light transmissivity comparable to a solar greenhouse across all film thickness range, while samples with a CF:PVA ratio of 0.2:30 (0.66%) are able to accomplish light transmissivity of solar and glass greenhouses as the thickness varies from a low of 0.6 mm to a high of 1.05 mm. Whereas samples with a CF:PVA ratios of 0.3:30 (1%) and higher have wide ranging light transmissivity from 70% down to 23%. Designing films at these CF:PVA ratios would require a close monitoring of the achievable light transmissivity at difference desired film thickness. To determine a film with acceptable light transmissivity for use as building material for agricultural greenhouse, while having good edge-to-edge resistance for infrared applications requires further study of the relationship between the two. Figure 7 shows the relationship between light transmissivity and block resistance for the various samples at different CF:PVA ratios with increasing film thickness.

Table 3: Sample calculations for Sample-03 CF:PVA=0.3:30 (1%) at LT=0.8 mm.

Relationship	Equation	R^2	Calculate Value
BR vs. TH	$BR_{TH,03} = 445.72 * TH_{03}^2 - 1341.3 * TH_{03} + 1207.7$ (Eqn. 1)	1	$BR_{TH',03}$=419.9208 Ω
LT vs. TH	$LT_{TH,03} = -455.67 * TH_{03}^3 + 1038.8 * TH_{03}^2 - 839.65 * TH_{03} + 298.47\ (Eqn.2)$	1	$LT_{TH,03}$= 58.2790%
LT vs. BR	$LT_{BR,03} = 0.0248 * BR_{03} + 51.628\ (Eqn.3)$	0.9878	$LT_{BR,03}$=62.0420%
MR vs. LT	$MR_{LT,03} = -0.1997 * LT_{03}^2 + 27.325 * LT_{03} - 596.7\ (Eqn.4)$	0.9885	MR_{LT03}=311.5902

BR denotes Block Resistance, TH denotes film Thickness, LT denotes Light Transmissivity, and MR denotes Material Resistivity. R2 is an indicator of the fitting degree of the equation to the data set when performing linear regression. A value of 1 indicates a fit of high reliability.

Table 4: Distribution of carbon fibers of different content in polyvinyl alcohol film formation.

Sample No.	**CF (g):PVA (g) (CF (g)/PVA(g) x%)**	**Solution Quantity in every mold (mL)**	**Measured TH (mm)**	**Edge-to-Edge Resistance (Ω)**	**Block Resistance (Ω)**	**LT (%)**	**Material Resistivity ρ (Ω•mm)**
	80.0	0.6020	945,000.00	945,000.00	84.89	568,890.00	
	0.1:30	100	0.7525	756,000.00	756,000.00	80.08	568,890.00
Sample-01	0.33%	120	0.9030	604,800.00	604,800.00	73.63	546,134.40
		140	1.0535	483,840.00	483,840.00	70.70	509,725.44
Mean		110	0.82775	697,41000	697,410.00	77.33	548,409.96
		80.0	0.6020	1,260.00	1,260.00	75.08	758.52
	0.2:30	100	0.7525	1,008.00	1,008.00	72.22	758.52
Sample-02	0.66%	120	0.9030	806.40	806.40	69.29	728.18
		140	1.0535	645.12	645.12	67.07	679.63
Mean		110	0.8278	929.88	929.88	70.92	731.21
		80.0	0.6020	560.87	560.87	70.07	337.64
	0.3:30	100	0.7530	448.69	448.69	60.72	325.64
Sample-03	1.00%	120	0.9030	358.95	358.96	59.83	324.14
		140	1.0540	287.16	287.17	55.08	302.53
Mean		110	0.8280	413.92	413.92	61.425	322.49
		80.0	0.6020	430.25	430.25	62.36	259.01
	0.6:30	100	0.7530	344.20	344.20	59.98	259.01
Sample-04	2.00%	120	0.9030	275.36	275.36	58.74	248.65
		140	1.0540	220.28	220.29	56.98	232.07
Mean		110	0.8280	317.52	317.52	59.52	249.69
		80.0	0.6020	380.56	380.56	51.04	229.09
Sample-05	1:30	100	0.7530	304.44	304.45	45.25	229.09
	3.33%	120	0.9030	243.55	243.56	28.22	219.93
		140	1.0540	194.84	194.85	23.08	205.27
Mean		110	0.8280	280.85	280.85	36.89	220.85

TH denotes thickness of the film. LT denotes light transmissivity under LED lightning at average 5,395.5 Lux. Edge-to-Edge Resistance (Ω) is comparable to Block Resistance (Ω) as the samples are square shaped. Specimen size is 200 × 200 mm and carbon fiber length is 3 mm.

Figure 9 shows the relationship of Light Transmissivity vs. Block Resistance for the various samples. As shown, light transmissivity increases with block resistance. Higher block resistance is a result of lower CF content, which increases the film's transparency as the ratio of the PVA material, which has high light transmissivity property, increases.

Figure 10 shows the relationship of Material Resistivity vs. Light Transmissivity. In general, material resistivity increases with the increase of light transmittance. This is in agreement with the results shown in Figure 11, as material resistivity is a function of carbon percentage content of fiber content which blocks light transmission through the PVA based films.

Figures 7-10 also presents the various design equations obtained through regression analysis, which allows us to match corresponding film thickness and required CF:PVA ratios to desired Light Transmissivity and Resistance values. As the Light Transmissivity and Resistance of the film is highly dependent on the film thickness, which in turn is affected by the CF:PVA ratios, a set of equation is required for each specific CF:PVA ratio. One example of the design equations are as follows for the CF:PVA of 0.3:30 (1%) film sample:

$$BR_{TH,03} = 445.72 * TH_{03}^2 - 1341.3 * TH_{03} + 1207.7 \quad (1)$$

$$LT_{TH,03} = -455.67 * TH_{03}^3 + 1038.8 * TH_{03}^2 - 839.65 * TH_{03} + 298.47 \quad (2)$$

$$LT_{BR,03} = 0.0248 * BR_{03} + 51.628 \quad (3)$$

$$MR_{LT,0.3} = -0.1997 * LT_{03}^2 + 27.325 * LT_{03} - 596.7 \quad (4)$$

Where BR is the Block Resistance in Ω, TH is the film thickness in mm, LT is light transmissivity in %, and MR is material resistivity in Ω.mm.

Eqns. (1) and 2 allows for the calculation of Light Transmissivity and Block Resistance given the film thickness, whereas Eqns. (3) and 4 relate Light Transmissivity to Block Resistance and Material Resistivity to Light Transmissivity. As the thickness of a film can be controlled in an industrial manufacturing setting, the equations can be used to determine the achievable block resistance and light transmissivity. Table 4 shows the sample calculated values using this set of equations.

From Table 3, it is observed that while the Light Transmissivity calculated using Eqns. (2) and (3) differs by 3.763%. This is due to the less-than-ideal R^2 value in the linear regression when obtaining Eqn. (3). After we are done with all the general testing, certain specs are

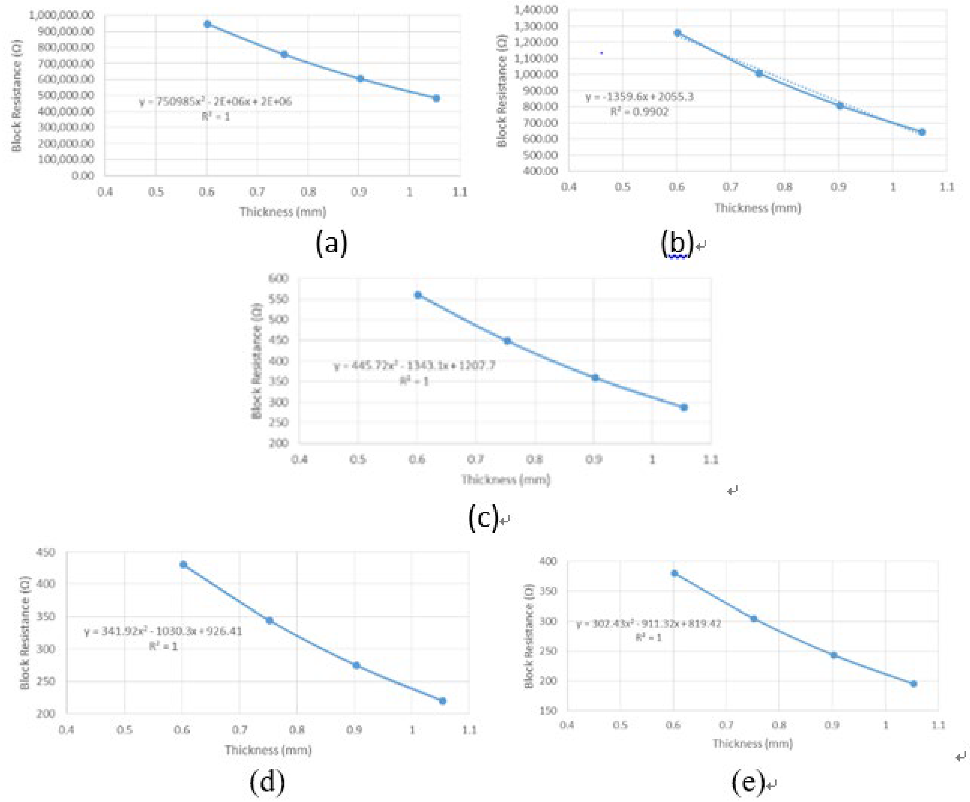

Figure 7: the relationship on the sample for Block Resistance (Ω) vs. Thickness (mm): (a) Sample-01: CF:PVA of 0.1:30 (0.33%), (b) Sample-02, CF:PVA of 0.2:30 (0.66%), (c) Sample-03, CF:PVA of 0.3:30 (1%), (d) Sample-04, CF:PVA of 0.6:30 (2%), and (e) Sample-05, CF:PVA of 1:30 (3.33%).

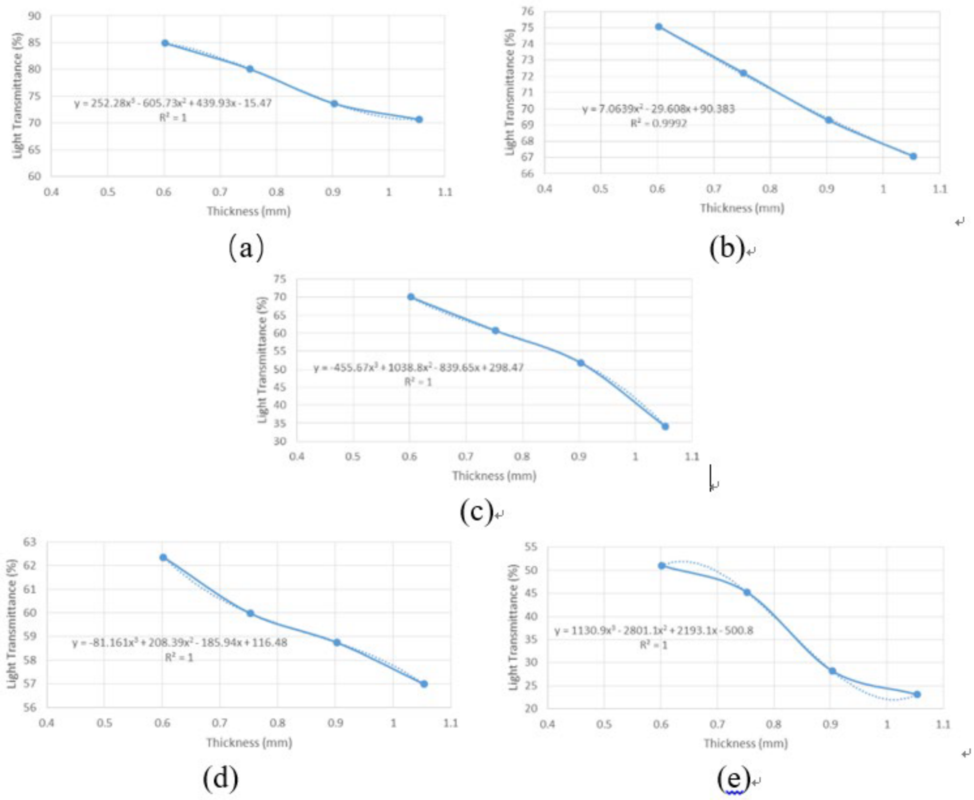

Figure 8: the relationship on the sample for Light Transmissivity vs. Thickness with equation for CF-PVA: (a) Sample-01: CF:PVA of 0.1:30 (0.33%), (b) Sample-02, CF:PVA of 0.2:30 (0.66%), (c) Sample-03, CF:PVA of 0.3:30 (1%), (d) Sample-04, CF:PVA of 0.6:30 (2%), and (e) Sample-05, CF:PVA of 1:30 (3.33%).

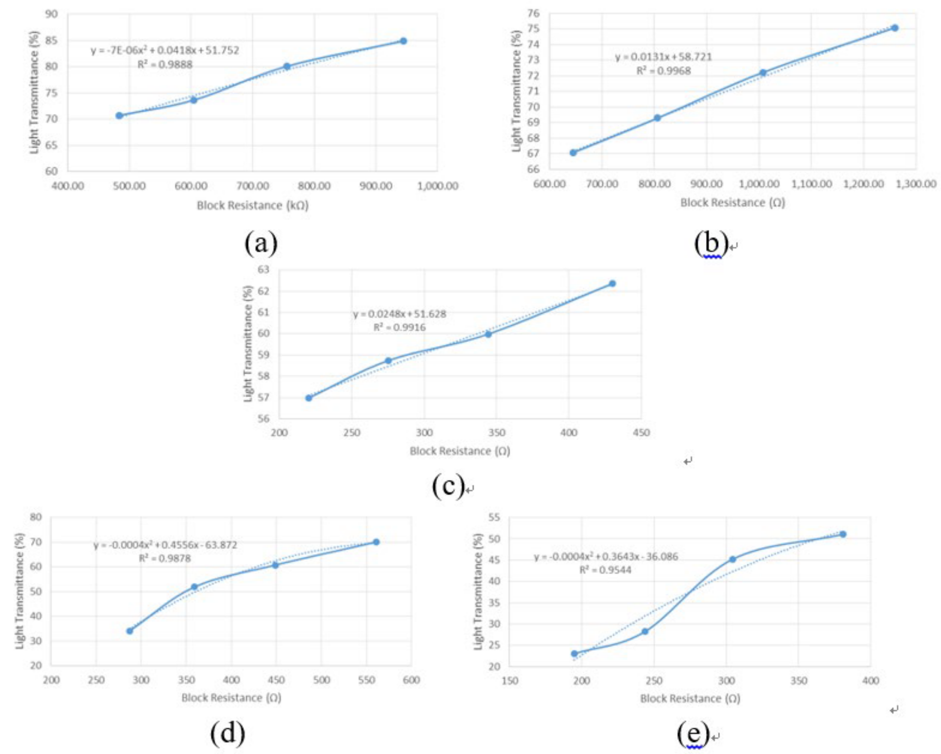

Figure 9: the relationship on the sample for Light Transmissivity vs. Block Resistance with Equations for CF-PVA. (a) Sample-01, CF:PVA of 0.1:30, (b) Sample-02, CF:PVA of 0.2:30, (c) Sample-03, CF:PVA of 0.3:30, (d) Sample-04, CF:PVA of 0.6:30, (e) Sample-05, CF:PVA of 1.0:30.

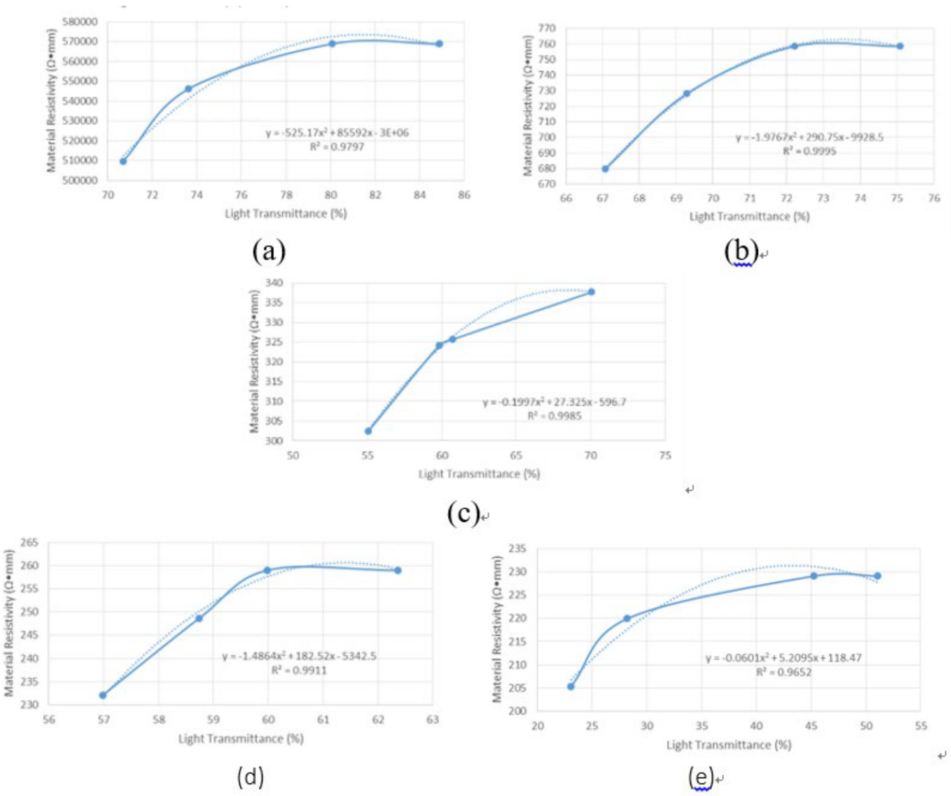

Figure 10: the relationship on the sample for Material Resistivity vs. Light Transmissivity with Equations. (a) Sample-01, CF:PVA of 0.1:30, (b) Sample-02, CF:PVA of 0.2:30, (c) Sample-03, CF:PVA of 0.3:30, (d) Sample-04, CF:PVA of 0.6:30, (e) Sample-05, CF:PVA of 1.0:30.

Note: R2 is the percentage of the dependent variable variation that a linear model explains.

R2 = variance explained by the model / total variance. Larger R2 typically means the regression model has a better fit to the data.

Figure 11: the process of fabricating PVA-CF transmittance conductive film.

chosen to design the final film used for the agricultural greenhouse. As have obtained the condition on PVA with CF:

$$0.33\% < CF/PVA < 3.33\% \quad (5)$$

CF/PVA < 0.33% which the conductivity is too low, the film cannot meet need of infrared (the Edge-to-Edge Resistance is low for radiation far-infrared on greenhouse), and the CF/PVA > 3.33% which the transmissivity is too low, the film cannot meet need of the transmissivity (the transmissivity is low for crop growth needs on greenhouse).

In the experiment shown using transparent conductive film in agricultural greenhouse, installed transparent conductive at 2600 W (72 W/m^2), when the air average temperature in one month 15.03°C to 3.8°C, warming the greenhouse with PVA-CF light transparent conductive film on 12 hours every, the average temperature in the greenhouse keep 12.33°C to 10.06°C. Illustrates the PVA-CF light transparent conductive film be applied for warming greenhouse that it is can be use (see the Table 5 in Supporting Information).

Experimental Section

Experimental Setup

PVA-CF films can be manufactured using either solution salivation method (wet method) or extrusion blown film method (dry method). In this study, the wet method is used. In the industry, PVA films are generally manufactured with the use of a casting machine with roller press. For the initial experimental work on determining the feasibility and properties of the PVA-CF films, a wet method is adapted for preparing the films (see Figure 11). First, CF filament is mixed in diluted PVA and glycerin solution. The addition of glycerin ensures that the resulting film is flexible and not rigid. The mixture is then slowly blended for up to 2.5 hours to ensure the CF filament is dispersed evenly. The mixture is then casted in a mold and left for air drying up to 48 hours in ambient room temperate. The resulting product is a thin and flexible PVA-CF transparent conductive film. Note that this method is only suitable for fabricating small size films.

For the application of the developed film for agricultural greenhouse, two custom made specialized fabrication machines are constructed to produce the film in larger sizes. The first machine is used for fabrication of the basic flexible conductive PVA-CF films, while the second machine is then used to apply metal copper foil strips for electric current delivery to the film and to laminate the film to provide electrical insulation and ensure the durability of the film. The two fabrication machines are respectively shown in Figures 12 and 13.

As shown in Figure 12, to produce the basic flexible conductive PVA-CF films, the mixture of CF filament in diluted PVA and glycerin solution is first blended in a mixer drum for 2.5 hours. The mixture is then pumped into a vacuum cavitation cylinder that removes all air bubbles from the mixture solution before the mixture is pumped squirted through a horizontal slit funnel onto a 10-meter length conveyor steel belt that is heated at 80°C. The mixture which is spread over the metal hot plate is then then left to air dry as it is slowly transferred along the heated steel belt for up to 5 minutes before being winded into a roll.

Table 5: the data of Test warming temperature in greenhouse at morning 10:00 and night 10:00.

Date (11/2011)	In outside greenhouse Air Temperature		Test warming Temperature in greenhouse	
	The Highest	**The Lowest**	**Am 10:00**	**Pm 10:00**
01	15°C	6°C	12°C	8°C
02	16°C	9°C	12°C	9°C
03	20°C	9°C	15°C	10°C
04	22°C	11°C	16°C	11°C
05	21°C	14°C	16°C	16°C
06	19°C	12°C	16°C	12°C
07	14°C	-3°C	12°C	8°C
08	5°C	-1°C	10°C	8°C
09	10°C	2°C	8°C	8°C
10	12°C	3°C	10°C	8°C
11	11°C	2°C	9°C	8°C
12	13°C	2°C	10°C	8°C
13	17°C	3°C	12°C	12°C
14	17°C	4°C	12°C	12°C
15	15°C	4°C	12°C	12°C
16	15°C	5°C	13°C	12°C
17	18°C	7°C	14°C	12°C
18	20°C	6°C	16°C	14°C
19	18°C	8°C	16°C	14°C
20	18°C	10°C	16°C	12°C
21	11°C	0°C	12°C	12°C
22	3°C	-3°C	10°C	8°C
23	9°C	-1°C	7°C	8°C
24	13°C	-2°C	12°C	8°C
25	14°C	-1°C	12°C	8°C
26	12°C	-1°C	12°C	8°C
27	13°C	4°C	12°C	8°C
28	14°C	5°C	12°C	10°C
29	16°C	2°C	14°C	10°C
30	6°C	-2°C	10°C	8°C
Mean	15.03°C	3.8°C	12.33°C	10.06°C

Note: warming time night 10:00 to next morning 10:00 every day.

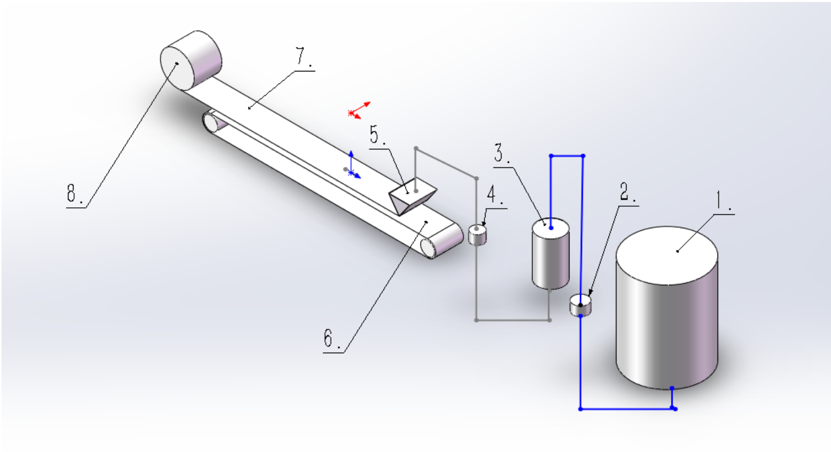

Figure 12: Fabrication machine for basic flexible conductive PVA-CF. 1: Mixer drum for mixing and blending of PVA, CF and glycerin. 2 & 4: pump. 3: Vacuum cavitation cylinder. 5: Horizontal slit funnel. 6: Heated conveyor steel belt. 7: PVA-CF film. 8: Winding machine.

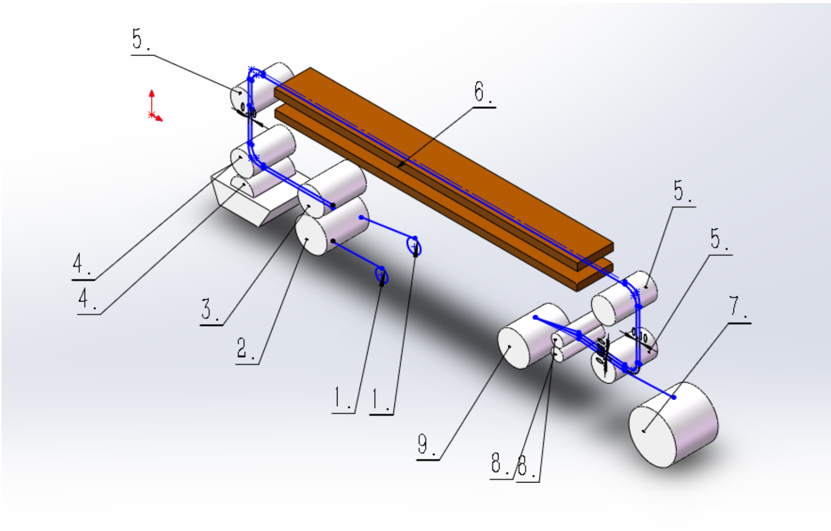

Figure 13: Modified food packaging machine for application of metal copper foil strips and protection laminate. Blue line indicates the feed path of the film. 1: current-carrying, 2: PVA-CF film roller, 3: Top laminate. 4: Glue applicator roller box. 5: Guide roller. 6: Forced convection oven. 7: Button laminate. 8: Hot drum, 9: Winding machine.

PVA-CF films are fabricated by infusing CF filaments in PVA substrate. CF is electrically conductive, and the mixture of the two material allows for the casting of an electrically conductive film.

For the application of the metal copper foil strips and protection laminate, a modified food packaging machine was used (see Figure 13). First, the current carrying metal copper foil strips are aligned and rolled onto the edges of the roll of conductive PVA-CF film. The top laminate is then applied onto the aligned copper foil strips and PVA-CF film to form a 2-layer film. Next, the 2-layer film is fed through a glue applicator roller box and then sent to a forced convection oven for drying. Finally, the bottom laminate is applied to the 2-layer film and sent through two hot drums for the final pressing to obtain the finished laminated film. The result is a durable PVA-CF film that can be applied directly in agricultural greenhouse setting.

For rural application of the film in agricultural greenhouses, aluminum air batteries are fabricated and applied for testing purposes. I have made an aluminum air batter which compose in 200 single aluminum air batteries with 12 V and 20 mA on PVA-CF transparent conductive film for 7 weeks now up till 01/Jan/2022: capacity = 20 mA x 24 hour x 7 days x 7 weeks = 235.2 Ah, see Figure 14. This battery be made at Carbon Rod as anode and aluminum sheet as cathode in size Ø18 mm by 200 mm. A single batter is 0.6 V and 0.2 mA, to drive a 1000 mm by 500 mm PVA-CF transparent conductive film (Edge-to-Edge is 480 Ω).

Experimental Method

Prior to the actual fabrication of the films for testing, an initial experiment to determine a suitable CF filament length is performed. 0.3 g of CF filaments of 3 mm, 6 mm and 10 mm length are respectively cut and mixed with 30 g of PVA, 15 ml of glycerin and 385 ml of distilled water. The solution is blended for two hours and the left to settle for 2 hours for the air bubbles disperse. The uniformity of the CF filament dispersion in the mixture is then observed. Next, 3 samples were casted using the 3 mixtures and the CF filament dispersion is further observed in the produced films.

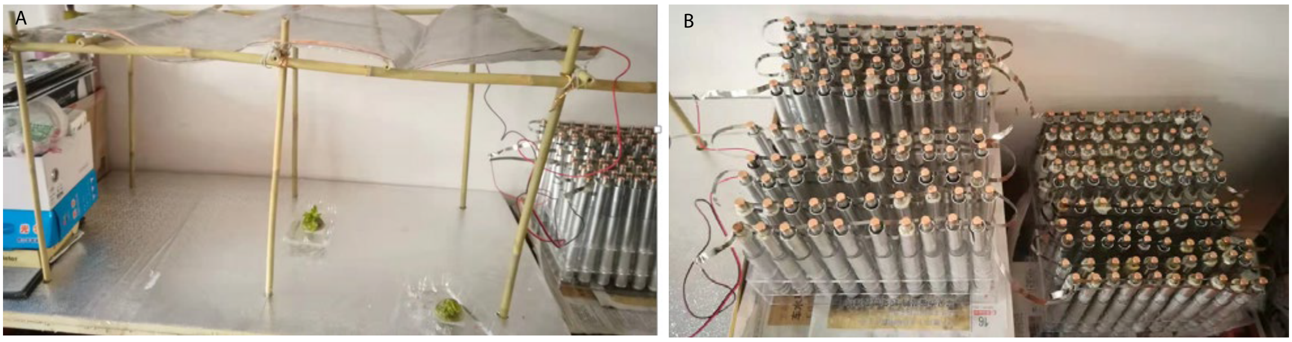

Figure 14: Aluminum-air batteries with K_2SO_4 electrolyte (a) compose in 200 single aluminum air batteries with 12V and 20 mA for PVA-CF transparent conductive film, (b) To parallel connect 10 single battery and series connect 20 battery groups and all in one.

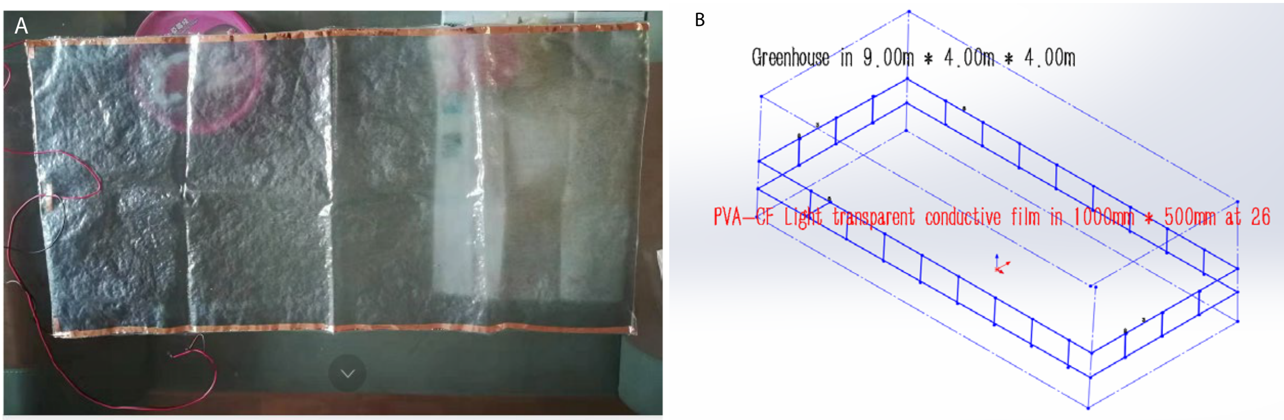

Figure 15: The PVA-CF Light Transparent conductive film be installed on greenhouse wall. (a) PVA-CF transparent conductive film. (b) Installation of 26 sheets of PVA-CF to the custom built agricultural greenhouse.

Next, using the fabrication machines, various 200 mm by 200 mm samples using 3 mm CF filaments at CF to PVA ratio of 1:100 are fabricated. The samples are tested for light transmissivity using LH – 206 Optical Transmittance Meter made in Tianjing China.

To determine if the films are suitable for both heating and building usage in agricultural greenhouses, various film samples are fabricated at different CF to PVA ratios of 0.1:30 (0.33%), 0.2:30 (0.66%), 0.3:30 (1.0%), 0.6:30 (2.0%) and 1.0:30 (3.33%). The thickness, edge-to-edge resistance, block resistance, light transmissivity and material resistivity are observed.

Finally, to determine the effectiveness of the fabricated conductive film in agricultural greenhouse, films were fabricated at CF to PVA ratio of 0.6:30 (2.0%). The film has the following properties: edge-to-edge resistance of 480 Ω, power rating of 100.83 W at 220 V, and dimension of 1000 mm x 500 mm (see Figure 15a). A custom 9 m x 4 m x 4 m agricultural greenhouse is used as the test bed of the films. A total of 26 sheets of the fabricated film is applied to the side walls of the greenhouse (see Figure 15b) and the temperature difference is observed.

Supporting Information

Please find below in Tables 4 and 5.

Conclusion

The newly developed film has an average Edge-to-Edge Resistance of 2069.58 Ω (Table 4), light transmittance of 75.75% (Table 4) and has a heating capability of 23.38 W/m^2 (220^2/2069.58 Ω) via far-infrared light (sample size is 200*200 mm and voltage in 220 V), which is far from meeting the temperature requirements of crop growth. To solve this problem, one is to increase the content of carbon fiber, sacrifice the transmittance, increase the power of the film, to improve the infrared radiation capacity; Second, increase the heating time to increase the accumulation of the overall infrared radiation.

From Table 3 shows, through setting the facts, the Block Resistance reach 419.9208 Ω, heating capability of 115.26 W/m^2 (220 V/419.9208 Ω) via far-infrared light, and the light transmissivity reach 58.2790%, It can basically meet the requirements of agricultural greenhouse lighting rate and suitable crop growth.

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