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Review

Sustainable Greenhouse Covering Materials with Nano- and Micro-Particle Additives for Enhanced Radiometric and Thermal Properties and Performance

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Abstract: This review aims to provide a comprehensive overview of nano- and microscopic materials that can provide thermal radiation insulation without reducing visible light transmittance, thereby reducing heat loss and conserving energy in greenhouses. We also reviewed the radial and thermal properties of greenhouse covering materials. Fillers, colorants, reinforcers, and additives, as well as glass, plastic film, and plastic sheet materials, were discussed. Additionally, by searching for keywords like insulation film, insulation agent, and infrared insulation, compounds based on graphene and fullerene as well as phase transition materials (PCMs) that may be used for radiation insulation, we proposed their potential use in greenhouse covers. They can be divided into semi-transparent photovoltaic (PV) materials, zinc oxide-based film fillers, and silica filter films. We discussed the radiation heat insulation and light transmission characteristics of these materials. Nano-synthesis techniques were also investigated. Based on latest advances in the literature, future developments in the micro- and macroscale synthesis of nanomaterials will enable additional innovations in covering materials for greenhouse structures. A limiting factor, though, was the high sensitivity of PVs to external climatic and meteorological variables. The ability of materials used to make greenhouse covers to control the microclimate, reduce CO_2 emissions, use less energy, and increase agricultural productivity, however, cannot be disputed. Similar to this, a thorough examination of the uses of various greenhouse technologies reveals that the advancements also have financial advantages, particularly in terms of reducing greenhouse heating and cooling expenses. The PCMs, which decreased greenhouse-operating costs by maintaining constant ambient temperatures, provide ample evidence of this.

Keywords: greenhouse; covering; cladding; nano-additives; thermal properties; radiometric properties; insulation film; insulation agent; infrared insulation

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1. Introduction

In recent years, the use of greenhouse surfaces has increased significantly all around the world. According to Standard EN 13031-1:2001 [1], which controls greenhouse design and construction in Europe, a greenhouse is “a structure used for the cultivation and protection of plants and crops that exploits the transmission of solar radiation under controlled conditions to improve the environment of growth, with dimensions that allow people to work inside”. The greenhouse is like a solar collector; it collects solar energy and uses it to promote plant growth. The amount of solar radiation that enters a greenhouse depends on a variety of elements, such as ground-reflected radiation, the shape and orientation of the greenhouse, the type of structure, the transmittance, absorption, and reflection of the covering material, the size and location of the opaque structure, dust on the cover, and cover condensation.

Minimizing heat loss is necessary to keep the greenhouse's temperature in the proper range [2,3]. The greenhouse's thermal energy balance considers ground heat loss, ventilation, storage exchange, thermal radiation, and conduction when estimating heat loss (see Figure 1) [4]. Moreover, the covering material is the most important of the previously mentioned components because its characteristics most significantly affect the microclimate in a compact space. Greenhouse cover, as well as its structural elements, soil, and crop, contribute to solar radiation absorption and affect latent heat generation [2,3]. Glass, semirigid polymers, and plastic films are the most widely used greenhouse covering materials. In contrast to those in open fields, they vary crop growth conditions by protecting the crop from inclement weather and altering the greenhouse environment.

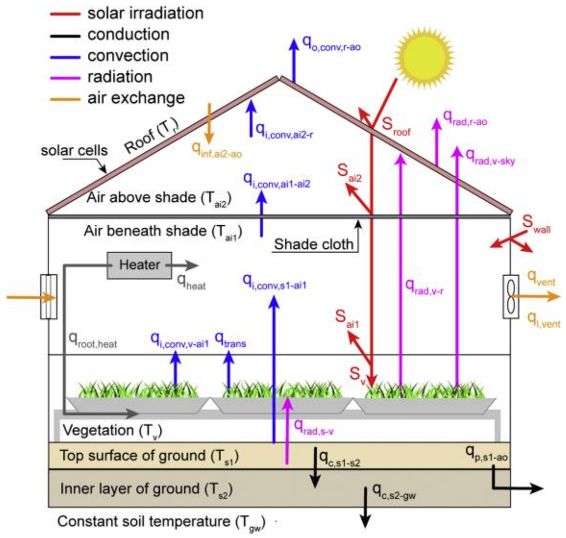

Figure 1. Energy fluxes in a greenhouse [4].

Covering materials allow solar light with visible and long infrared wavelengths to pass through, affecting greenhouse atmospheres [5,6]. The spectral distribution of solar radiation at the Earth's surface must be taken into consideration as a weighting function when calculating the radiometric coefficients of covering materials. Solar radiation is maximum at 500 nm in the PAR (Photosynthetically Active Radiation) zone (400 to 700 nm), where about 40% of the total energy is released, and more than 50% of the total energy is emitted in the near-infrared radiation (NIR) region (700 to 2500 nm) [7–9]. The transmissivity coefficient, which is evaluated in the wavelength range of 300 nm to 2500 nm, indicates the amount of overall solar energy that goes through the covering material. The transmissivity coefficient in the PAR range, which substantially impacts crop development and yield, indicates how much solar PAR radiation the covering material transmits [5,6]. The quantity of energy lost by long-wave infrared radiation from shielded portions will vary depending on how well the covering material transmits light at wavelengths longer than 3000 nm. However, at normal temperatures, the body's maximum energy emission ranges from 7500 to 12,500 nm [4,10]. Moreover, the air temperature inside the greenhouse is significantly influenced by the emissivity of the covering material, which measures the thermal radiative energy emitted in the long infrared radiation. The insulated environment will lose significant energy if the covering material has a high emissivity.

The greenhouse cover's radiometric properties are essential for lowering energy usage [5,6]. The greenhouse sector may become more lucrative, produce crops that are profitable, and use less energy to heat and cool the greenhouse by implementing cutting-edge covering materials. The use of covering materials that change the spectral distribution of solar light and thus affect plant development can replace the usage of agrochemicals. Research has focused on the radiometric characteristics of glasses and, more recently, the characteristics of plastic films, the most widely used materials for greenhouse covering [11–21].

Plastic films are the most widely used and cost-effective type of covering material. Various types of plastic films include PVC (polyvinyl chloride), EVA (ethyl vinyl acetate), and polythene (polyethylene), to name just a few. Because of continual developments in polymers, these covering materials are exceedingly adaptable and provide a wide range of performance options. Moreover, coatings may use various additives to provide plastic films with useful properties for increased greenhouse efficiency. Films can reflect long-wave infrared light to maintain interior heat at night or to block UV rays for chemical-free pest control. As a result, some plastic covering materials are colored. Micro and nano additives in the plastic determine the strength, ability to prevent heat loss, ability to prevent droplet formation, ability to transmit particular light wavelengths, and ability to prevent dust from adhering to the film. UV (290 to 400 nm) stabilizers and absorbers can help materials last longer, reduce the likelihood that they would affect greenhouse biological systems, and they may even be able to control some plant diseases. When infrared absorbers (700 to 2500 nm) are utilized, long-wave radiation is reduced, and heat loss is minimized [7–9]. When long-wave radiation (2500–40,000 nm) absorbers are employed, the greenhouse's components and plants lose less heat [22,23]. Surfactants reduce the surface tension of water, which disperses condensation, whereas antistatic compounds reduce the tendency for dust to accumulate on plastic sheets. Fluorescence can promote red light output, color pigments that alter the ratio of particular wavelength ranges can promote plant development, and glossy surfaces can deter insects.

The multilayer filmmaking method can be used to assemble thin layers of materials with different properties to produce excellent composite films. The attributes that can be improved are long-wave radiation absorption, creep (deformation over time), and toughness.

Moreover, the use of phase-change materials (PCMs) allows for passive and free winter heating of the greenhouse owing to their high energy storage density capabilities and their ability to store thermal energy in a constant temperature phase transition process [24]. PCM evens out temperature differences, especially in the spring and fall, which results in the plants being less stressed and leads to a greenhouse that uses a lot less energy overall. PCM uses latent heat fusion to passively warm the greenhouse. It keeps the greenhouse much warmer during the frigid winter evenings by passively storing heat from the sun during the day and releasing it again at night. The energy transfer that occurs during phase changes is used by materials that travel through them. A significant amount of energy is transferred each time a substance transitions between its phases—from solid to liquid to gas—because molecules must either link up or separate. Throughout the day, as PCM changes from a solid to a liquid, it absorbs the greenhouse latent heat of fusion. At night, the substance "freezes" once more, sending its energy back into the greenhouse where it gradually produces heat [24].

This review also includes a critical analysis of polymer-based greenhouse films with nano-additives to prevent heat loss. The primary subjects of this review will be the thermal radiation absorption and heat retention capacities of polymer-based greenhouse films. In addition to its mechanical characteristics, UV absorption, and VIS transmission, we will evaluate its additional qualities. These characteristics are essential for plant growth and greenhouse applications. For instance, keeping plants alive takes extraordinary mechanical properties while a shipment is transported in a greenhouse [25]. Rheological modification techniques are necessary for agricultural films [26]. Since UV radiation may impair the growth of plants and animals, greenhouses must absorb it [5,6]. The agricultural film's VIS transmittance must also satisfy the plant's lighting needs [27]. As civilization develops, there is a rising demand for environmentally friendly goods [28]. Therefore, it would be incredible if this film could be recycled [28]. Investigations will also be made into heat-insulating composite sheets' potential IR-blocking properties. The phonon oscillations of the silica and polymer particles are responsible for these composite materials' capacity to filter infrared light [29]. Thermal insulation can be improved by utilizing a complex network of IR reflection fillers made up of silica filler and a combination of silicates, carbonates, sulfates, and a borate. The infrared emissions of composite materials made of polymer and zinc oxide can also be explained using the Anderson localization approach. The "low-energy impurity band" and Anderson's limitation film phenomenon, both of which are attributed to the random lattice behavior of the zinc oxide particles in the composites, are most likely to blame for the problem of low-energy IR photons passing through the film.

As the manuscript is useful in terms of research and practice to engineers and agronomists, systematic background information is included to support readers in following this research.

2. Managing the Microclimate of the Greenhouse

The short-wavelength radiometric properties of the covering material directly impact the environment within a greenhouse. Studies have been done on the greenhouse's potential to theoretically and experimentally transfer solar radiation. This is because, among all factors, solar radiation—the largest source of free energy—has the most impact on crop productivity. Researchers utilized scale models to test the influence of a distinctive form of cover (Fresnel prism) fitted to the south roof of an E–W-oriented, single-span greenhouse [30]. Others investigated the relationship between a single-span greenhouse's length and width and its solar transmittance [31]. Numerous researchers (i.e., ref. [32–34]) have proposed ways to find out how a greenhouse's design and orientation affect its transmittance. One of many models' key objectives is to design a mechanism for understanding how variable greenhouse architecture and covering materials affect the overall solar radiation transmission. Solar transmissivity models calculate greenhouse transmittance as a function of the location of the sun during the day in order to imitate crop growth and greenhouse climate. These models all make some use of the radiometric features of the cover.

Because polyethylene transfers infrared radiation more effectively than glass, greenhouses hold onto less heat. As a result, all research on the greenhouse environment includes data on heat radiation exchange [35]. Researchers have used both fundamental (i.e., ref. [36]) and composite (i.e., ref. [37,38]) approaches to study the problem of heat radiation exchange in greenhouses. For heat radiation transfer, the covering material's radiometric properties are essential [39].

The "greenhouse effect", which happens when solar radiation enters a greenhouse through a transparent cover, is absorbed inside and then is unable to leave the greenhouse as thermal radiation because the cover is opaque to thermal radiation, was once thought to be the main cause of the development of the greenhouse microclimate. This action does not seem to have much of an effect on how the greenhouse environment develops. When there is no condensation, typical polyethylene films, which are widely employed to cover greenhouses, have a high heat radiation transmittance. Glass-covered greenhouses should have a different microclimate than polythene-covered greenhouses, but this is not the case. A greenhouse must be heated by air in contact with warm surfaces as it cannot absorb light energy. The roof, the structure that supports it, the floor, and any other surface or object that absorbs solar radiation make up these surfaces. The plants' temperature in a greenhouse is kept near to the air temperature because plants produce energy in addition to absorbing solar light [40].

Moreover, the temperature of the cover, support structure, and soil surface increases as some of the incident solar energy is absorbed during the day. The pace at which interior air warms up as it comes in contact with these surfaces varies depending on several characteristics, including the convective heat transfer coefficient, air exchange velocity, and temperature differential [3]. Radiative processes are referred to as the "greenhouse effect" to avoid confusion. The cover releases thermal energy into its surroundings to exchange energy with the inside and outside air during the night. The polyethylene cover loses so much heat during the cool, clear evenings after sunset that its equilibrium temperature is considerably lower than the greenhouse's air temperature. The air temperature within the greenhouse is lower than the air outside because of convection to the lower-temperature cover material. The cover's temperature remains below that of the air in the greenhouse because the rate of long-wave radiative heat loss from the cover outpaces its convective heat gains from the air [3,39,41].

The product is shielded from the elements by the greenhouse's plastic roof. It can make an ideal microclimate and offer weather protection with the cover. Because of their restricted design and poor heat capacity, coverings are inadequate insulators. The most desirable attribute of a covering material is insulation. The best cover should let all of the photosynthetically active radiation (PAR) through, taking into account both internal and external factors. It is also crucial to reduce the amount of solar radiation that enters the PAR. It must also perform effectively as an insulator. Due to their frequent incompatibility, no material currently combines all these qualities. Below we will evaluate the effects of state-of-the-art cover materials on greenhouse microclimate, enhancing their (radio)thermal performance using advanced nano- and micro-particle additive materials.

3. Evaluating the Effect of Cover Materials on Greenhouse Microclimates

3.1. Glass, Plastic Film, and Plastic Sheets as Greenhouse Covers

Glass, plastic, fiberglass-reinforced plastics, biodegradable paper, polycarbonates, poly(lactic acid), and polyhydroxyalkanoates (PHA) are the most typical greenhouse cladding materials [42–44]. Due to its strong PAR transmission and NIR reflectance, which lower the greenhouse's energy balance, glass is recommended as a cladding material. In contrast, plastic films and sheets have a higher NIR transmission rate [2]. Compared to glass, plastic materials often offer less IR shielding at night. Consequently, glass structures are required to house IR-sensitive plants. Fiberglass has an inferior optical clarity and light transmission despite having better mechanical properties [2].

Translucent solar panels [45], rigid polymethyl methacrylate (Plexiglass) [46], and Agril PP nonwoven fabric [2,47] are examples of secondary materials. The unique advantages, low cost, and widespread availability of plastics and glass are highlighted in the current study as factors supporting their ecological sustainability. On the one hand, plastics can be cast or molded into various shapes. Plastics can act as electrical insulators in addition to withstanding stress, acids, and bases [48]. They can withstand pressure. Three frequently utilized plastic sheeting types include polymethyl methacrylate, polycarbonate, and fiberglass [49,50]. Due to their high rates of UV light transmission, heat retention, and PAR transmission, plastics are frequently used [51].

When exposed to ethyl vinyl acetate, polyvinyl chloride (PVC), and polyethylene (PET), sheets lose some of their use and elasticity [49]. Even if it just adds three years to the lifespan of the buildings, the polymer sheets should be UV-resistant [44]. Without UV stabilization, photochemical processes and UV radiation degradation will cause polymer sheets to break down in three to five months. The usage of bioplastics, such as PHA, poly(lactic acid), and polycarbonates, which are synthesized by the fermentation of starch, may enhance the ecological sustainability of plastic films and sheets in addition to providing UV protection and stability [42,44]. Due to an unexpected increase in demand, researchers are becoming more and more interested in bioplastics. Around 460 million pounds of bioplastics were produced in 2019. However, not everybody decides to adopt them [42]. Petroleum-based polymers such as thermoplastic polyethylene (TPE) film, ethylene-vinyl acetate (EVA) film, three-layer co-extruded film, PVC, PP, and PET cost between EUR 0.77 and 0.81 to produce [52]. However, bioplastics are more expensive. Additionally, the cost of making one kilogram of PHA might be as high as EUR 12. Therefore, from a budgetary perspective, PLA and PHA plastic films are inappropriate. The advantages of material properties, including elongation at break, tensile strength, and glass transition temperature, outweigh any price increases. We could overcome the cost problems by finding, producing, and synthesizing novel materials.

According to researchers [50], PVC and glass-reinforced polyester have been shown to be efficient UV-resistant and UV-stable heat collectors. The poor mechanical, thermal, and aesthetic qualities of plastic cladding, such as insufficient insulation in cold or hot environments, decrease energy efficiency. Additionally, these materials have an unlimited optical potential [53].

Due to their suitable characteristics, plastics, as mentioned above, are frequently used in greenhouse covers in place of glass [49,50]. Because of their pollution and lack of biodegradability, thermoplastic and thermosetting polymers are bad for the environment [54]. This implies a trade-off between greenhouse plastic's effectiveness and environmental impact. Compared to plastic sheets and films, glass offers around 90% more thermal insulation [49,50]. Similarly, a study by [44] asserts that glass maintains heat more efficiently than other materials. When compared to standard glass, the advantages of heat shielding frequently outweigh the reductions in light transmission [44]. Due to the material's structural flaws and brittleness, which are caused by the broad grain boundaries, low tensile strength, and Young's modulus [55], installation is expensive and dangerous. Additionally, glass frequently has significant flaws that prevent it from being used as greenhouse cladding. However, low-temperature protection can be precisely controlled by modifying the material's properties.

3.2. Fillers, Colorants, Reinforcers, and Additive Materials

To enhance the properties of plastics, such as their ability to withstand heat, shed heat, produce droplets, and prevent dust from clinging to the film, functional additives, fillers, air bubbles, reinforcements (made of glass or carbon fiber), and colorants can be added [56]. For example, UV absorbers and stabilizing chemicals can stop plant degeneration in plants cultivated in greenhouses and exposed to UV-B radiation above 40 kJ/m^2 [57]. The additive also forecasts UV and IR transmission rates, which are expected to range from 0.70 to 0.90 for readily available materials [57]. The polymers' anti-fog and infrared additives stop harmful IR radiation from being transmitted and fog from forming [58]. Although some stabilizers enhance greenhouse cladding materials' mechanical and optical qualities, some stabilizers include dangerous heavy metals such as lead and cadmium [59,60]. The stabilizing agents for heavy metals pose a more significant threat to plants than the plants in greenhouses with PVC walls. Instead, the risk arises while recycling. Therefore, Gelatin, agar, and chitosan-based photocatalysts were formed as a result of the problem of heavy metal contamination and plant cytotoxicity [59,61].

To lessen the risk of UV damage and photodegradation posed to plastic films and sheets, stabilizers and additives such as carbon black and others change the optical characteristics of cladding materials [61]. As a result, structures made specifically for greenhouses are stronger. Hemp linen, jute burlap, and hemp burlap, among other fiber textiles for greenhouse walls and covers, are frequently used as reinforcement in composites made from bio-based plastics. Mechanical tests revealed that the composites constructed from hemp line had the highest ultimate tensile strength, percentage elongation, and resistance to creep deformation [62,63]. Reinforced hemp linen composites can be used to build greenhouse walls in place of concrete, porous clay blocks, and straw fibers because of their superior mechanical properties [64].

Plants are shielded from radiation harm by UV absorbers and additives, which slows the spread of pathogens and pests [54]. Infrared light absorbers minimize heat loss and short-wave emission. They typically have a wavelength between 700 and 2500 nm. Long wave absorbers (2500–40,000 nm) minimize heat loss from plants in greenhouses by absorbing long waves, similar to how light diffusers work. The surface tension of the plastic film and dust deposition is reduced by surfactants and antistatic compounds [65]. Red-emitting plastic greenhouse extensions provide stunning and vivid patterns and colors. This section covers the latter, marginally better greenhouse cladding materials.

The pigment volume fraction gets more efficient as the percentage of greenhouse gases rises (pigment volume fraction). Researchers have established the efficiency of diamond particle-based pigments in reducing radiation in greenhouse cladding materials [61]. When it comes to radiation management, HVAC systems are preferable to pigments. It is simpler to reflect incident light in the near-infrared range (800 to 2500 nm) while transmitting visible light with a shorter wavelength when pigments are made of TiO_2 and diamond particles [61]. These distinctive visual traits were absent from the pigments.

The effects of using pigments made from diamonds offers the following benefits. The greenhouse's ability to circulate heat starts to decline. Additionally, it offers sufficient light for photosynthesis. Pigments used for radiation-resistant greenhouse materials are made from different materials than diamond particles. The industry standard TiO_2 particles were found to be subpar to diamond particles. As the wavelength of the visible spectrum decreased, it became more distinct. However, the spectral region closest to infrared reflected the most light [61]. Due to its remarkable NIR scattering efficiency (d = 1.19 microns) and excellent VIS transmittance (95%), TiO_2 can replace diamond particles in low-cost applications [61]. Since transmittance declined as the particle diameter increased yet the scattering efficiency sharply increased, it is challenging to determine the precise link between particle size, transmittance, and scattering efficiency.

Transparent solar distillers (TSD), multipurpose greenhouse covering materials that use solar energy to desalinate water, have been synthesized using TiO_2 nanoparticles [62,66]. Products and materials for greenhouse cladding contain TSD pigments. The absorber layer's optical and thermal properties, particularly the rate of condensate formation and daily yield, were improved by the TiO_2 nanoparticle-based coating.

TiO_2 influences the optical properties of polymers and has biocompatible antibacterial properties that are critical for plant growth, which is hampered by bacterial and fungal infections [60]. To combat the spread of insect-borne plant diseases, such as tomato yellow leaf curl disease, new polymers with slow-release pesticide properties, such as LLDPE, have been synthesized [57,67]. The mobile release properties of a nanocomposite film containing halloysite have improved [67]. However, new polymer development poses a significant risk to public health [68]. These health issues have received insufficient attention. In the section that follows, we will look at the environmental issues caused by the materials used to cover greenhouses.

3.3. Greenhouse Covering Materials with Enhanced Properties

3.3.1. Radiometric Properties

The primary energy source on the Earth's surface is solar radiation. Because the human eye can only see light with a specific wavelength, most researchers agree that radiation is not light. The entire Earth's surface emits short-wave radiation during the day, as opposed to the atmosphere, which is constantly exchanging long-wave radiation. When a body's internal temperature changes, it emits thermal radiation (infrared electromagnetic radiation). The radiative flux of thermal radiation emissions is affected by temperature. Higher-temperature materials emit more energy than lower-temperature materials. As a result, there is a net energy loss, or the heated object cools gradually. While some greenhouse construction materials can transmit thermal radiation, others cannot. A greenhouse frequently maintains a higher temperature during the winter because materials that block thermal radiation store energy more efficiently than other materials. Therefore, it is crucial to consider the radiometric properties of the covering materials within the relevant light spectrum. The radiometric properties of the covering material inside the solar waveband must be investigated because the greenhouse consumes solar energy. The crop's spectrum sensitivity must be considered while monitoring photosynthetic activities and evaluating the radiometric properties of the cover.

Electromagnetic radiation can be transmitted, reflected, absorbed, and emitted by materials. Radiation can pass through transparent materials more readily than opaque ones. Transparent materials can transmit radiation both directly and inadvertently. Directly perpendicular radiation penetration does not significantly alter the radiation's initial trajectory. However, radiation beams disperse and flow in all directions as they travel through translucent or semi-transparent materials. The side of the material that is away from the radiation source exhibits weak shadows and isotropic radiation dispersion. To quantify a substance's transmission, haze is required. It is vital to stress the relevance of total radiant radiation, which includes both direct and diffuse radiation.

The electromagnetic theory allows for the prediction of a substance's radiometric properties. The derivations often overlook surface conditions and take assumptions for granted. Engineering applications rarely have an entirely smooth user experience; hence this limitation is crucial. The materials used to cover greenhouses mainly consist of plastic sheets and, to a lesser extent, glass, which are likewise strewn unevenly. Therefore, to evaluate the standard of covering material and provide a strong foundation for comparison, it is necessary to test several properties under controlled settings.

In contrast to an average solar transmissivity coefficient, which is the average transmissivity over a specific solar waveband weighted by the wavelength distribution density function in the solar spectrum, the spectral transmissivity of a material is the proportion of incident radiant flux transmitted at a given wavelength. Integrate $P_s(\lambda)$, the direct normal spectral irradiance at wavelength λ, to obtain the power between λ_1 and λ_2 in the sun's spectrum. The formula below is used to find the material's average solar radiation transmission coefficient.

$$\tau_s = \frac{\int_{\lambda_1}^{\lambda_2} \tau(\lambda) P_s(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} P_s(\lambda) d\lambda} \quad (1)$$

The transmissivity of the (λ) spectrum can be estimated using spectrophotometric data. ASTM standard E891 [69] and ISO standard 9050 [70] are two examples of standards that describe values for λ_1, λ_2, and the $P_s(\lambda)$ function.

By measuring the reflectivity of the spectrum, spectrophotometers may estimate the average solar reflectivity coefficient, or ρ. When τ and ρ are known, Equation (2) can be utilized to get the average solar absorption coefficient α [71].

$$\alpha + \tau + \rho = 1 \quad (2)$$

The emissivity coefficient is a measure of the difference between radiation actually emitted by a body and the emissive power of a black body at the same temperature [37]. The body's absorption coefficient and this ratio are the same. The general behavior of the material across the complete wavelength range is reflected by these two coefficients. The ratio of a body's monochromatic emissive power to a black body at the same wavelength and temperature is known as monochromatic emissivity. The temperature and radiation wavelength of a substance affect its monochromatic emissivity. When a body's monochromatic (spectral) emissivity is constant or when both its monochromatic emissivity and emissivity coefficient are wavelength-independent, the body is said to be a grey body. Real surfaces are not equally scattered like ideal surfaces; hence the radiation's intensity is not diffused consistently. Various surfaces absorb heat radiation differently depending on the surface and its surroundings. Regarding monochromatic radiation, the following assertion is accurate:

$$\varepsilon(\lambda) = \alpha(\lambda) \quad (3)$$

As a result, the absorption spectrum of a grey body remains constant. The wavelength-independent properties of emissivity and absorbance are unaffected by temperature. This is risky due to the likelihood that natural surfaces may not always reflect grey body behavior. Given that it may be tricky to define surface behavior exactly, the grey body approach is reasonable and uncomplicated. In the real world, indirect measurements of monochromatic normal emissivity and the emissivity coefficient over a range of wavelengths can be obtained using spectrophotometric data and estimates of absorption as a function of wavelength.

According to studies [72], the wavelength impacts the quantum photosynthesis process. To establish the effective quantum transmittance, or PAR transmittance, between 0.4 and 0.7 µm, the photosynthetic weighting factor $D(\lambda)$ must be estimated [73]. The

PAR transmissivity coefficient for perpendicular radiation events is computed using the formula below.

$$\tau_p = \frac{\int_{\lambda_1}^{\lambda_2} \tau(\lambda) P_s(\lambda) D(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} P_s(\lambda) D(\lambda) d\lambda} \tag{4}$$

Integration takes place inside the band of photosynthetic action. The weighting factor, $D(\lambda)$, for photosynthetic activity can be computed using [74] the quantum yield relationship.

If it is known that the average solar radiation scattering transmissivity coefficient depends on the azimuth and altitude angles of the incident direct solar energy, the following formula can be used to calculate the coefficient:

$$\tau_f = \frac{\int_{\beta=0}^{\pi/2} \int_{\gamma=0}^{2\pi} \tau_g(\gamma, \beta) G(\gamma, \beta) \sin\gamma \cos\beta d\gamma d\beta}{\int_{\beta=0}^{\pi/2} \int_{\gamma=0}^{2\pi} G(\gamma, \beta) \sin\gamma \cos\beta d\gamma d\beta} \tag{5}$$

The phrases $\tau_g(\gamma, \beta)$ and γ, β correspond to the intensity and transmissivity of diffuse solar irradiation, respectively, and rely largely on azimuth and altitude.

The diffuse solar irradiance $G(\gamma, \beta)$ has been estimated using a variety of approaches [75]. However, the majority of models compute the entire spectrum. It is simple to calculate the average (full spectrum) transmittance coefficient to distribute solar energy in both cloudy and clear sky conditions. Researchers (i.e., [76,77]) recommended the functions $(1 + 2\sin\beta)/3$ and $(1 + 3\sin\beta)/4$ for the radiation distribution in a "standard" overcast sky, even though $G(\gamma, \beta)$ should be constant (i.e., independent of β and γ). The diffuse radiation dispersion for a clear sky would be proportional to $1/\sin\beta$ since it is the largest in the direction where the total air mass (the air mass function) is greatest (the air mass function). In 1971, researchers added the sun's azimuth and height to the clear-sky diffuse radiation distribution [78]. Based on the radiation distribution formed by the equation's function, the aforementioned functions can be utilized to compute the transmissivity to diffuse solar radiation.

The formula below, which is equivalent to the prior equation, can be used to find the transmissivity coefficient of a greenhouse covering material.

$$\tau_l = \frac{\int_{\lambda_1}^{\lambda_2} \tau(\lambda) P_T(\lambda, T) d\lambda}{\int_{\lambda_1}^{\lambda_2} P_T(\lambda, T) d\lambda} \tag{6}$$

The function $P_T(\lambda, T)$ in the equation above represents the radiant excitation in the long-wave spectral area. The radiant flux density at a surface can be expressed using Planck's law as $P_T(\lambda, T)$, where T is the surface's black body emissive power. Based on the Planck equation, this description of the band $[\lambda_1, \lambda_2]$ makes it abundantly evident that it is firmly related to a particular material temperature. Since the coefficient of transmissivity is generally not unduly sensitive to temperature, measurements of transmissivity are routinely performed at 300 K in the absence of a reference temperature.

If the opaque body's spectral reflectance between 5 and 25 µm is known, one may use the following equation to compute its average normal emissivity coefficient. Figure 2 shows the spectral emissivity of glasses.

$$\varepsilon_t = \frac{\int_{\lambda_1}^{\lambda_2} \{1 - \rho(\lambda)\} P_T(\lambda, T) d\lambda}{\int_{\lambda_1}^{\lambda_2} P_T(\lambda, T) d\lambda} \tag{7}$$

When λ_1 is equal to 5 µm and λ_2 is equal to or less than 25 µm, the $P_T(\lambda, T)$ function is provided by the equation above. Using a variety of approaches, coated glass can be identified from uncoated glass based on the divergence from the usual hemispherical emittance [79].

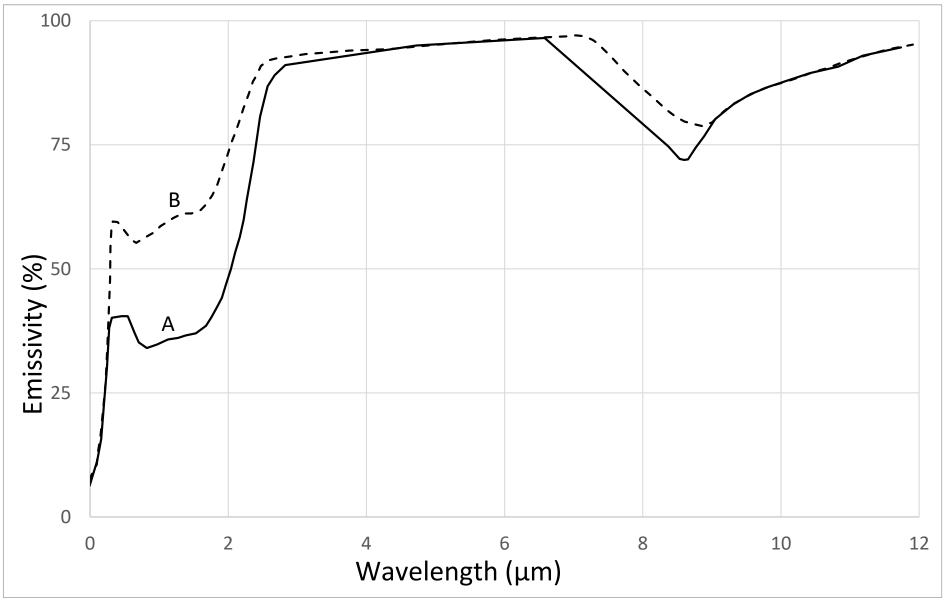

Figure 2. The spectral emissivity of glass, where A and B the spectral for two common glasses [80].

The following ratio, or the ratio for red to far-red irradiance, was proposed by [81] for testing the effectiveness of freshly synthesized fluorescent or bright plastic sheets:

$$\xi = \frac{G_{660}}{G_{730}} \tag{8}$$

G_{660} and G_{730} indicate the photon fluence rates at 660 and 730 nm in the 10 nm wavelength band centered on these wavelengths. A plant's level of active morphogenesis can be assessed from this ratio. While a lower ratio reduces leaf area and branching while enhancing stem elongation and apical dominance, a higher ratio enhances plant branching while decreasing stem extension [82]. The ratio value can be employed to determine how the luminous covering material affects plant growth and development in a greenhouse setting.

3.3.2. Thermal Properties

The water vapor transfer coefficient mainly handles latent heat transmission. The heat flow density through a unit thickness of an infinite slab of a homogeneous material in a direction perpendicular to the surface brought on by a unit temperature difference is known as the coefficient of thermal conductivity, or k, under steady-state conditions. The equation reads as follows:

$$k = QL/A(T_1 - T_2) \tag{9}$$

The symbols T_1 and T_2 represent the sample's temperature difference, heat flow, research area (Q, L, and A), and hot and cold surfaces, respectively.

The quantity of heat that passes from a greenhouse covering to its surroundings when there is a unit temperature differential between the covering and the surrounding air is measured by the convective heat transfer coefficient, abbreviated as h. The calculation is done as follows:

$$\begin{aligned} h_h &= Q/A(T_h - T_1) \\ h_c &= Q/A(T_2 - T_c) \end{aligned} \tag{10}$$

In these equations, the subscripts h and c stand for heated and cold surfaces, respectively. Figure 3 shows different variations of heat transfer coefficient inside the greenhouse covering materials' surface according to various authors.

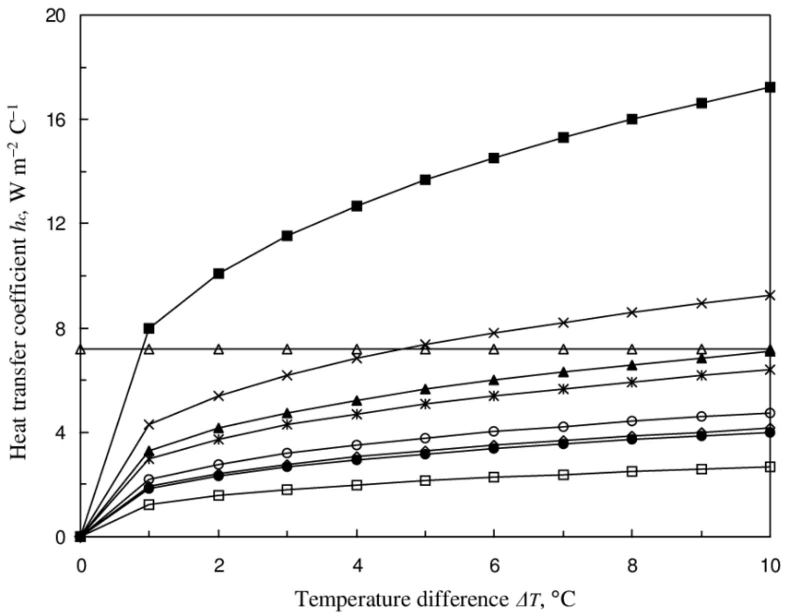

Figure 3. Heat transfer coefficient inside greenhouse cover surface (data from literature and different authors) [83].

The whole quantity of heat that flows through a composite material via conduction and convection is measured by the overall coefficient of heat transfer, often known as the K value. The equation reads as follows:

$$K = \frac{1}{\frac{1}{h_h} + \frac{1}{h_c} + \sum_j \frac{d_j}{k_j}} \quad (11)$$

The thickness, thermal conductivity, and convective heat transfer coefficients of the material's inner (typically hotter) and outer (often cooler) surfaces are indicated by the letters d_j, k_j, and k_j, respectively. Because heat radiation exchange is not taken into consideration in the preceding equation, the expected value of the coefficient K would be lower than the actual value if there are large thermal radiation exchanges. Condensation is not taken into account in this calculation.

By incorporating thermal radiation exchanges into the previously stated equation and guaranteeing that the coefficients h_h and h_c account for both thermal and radiation heat transfer, researchers were able to establish the K values of a range of greenhouse-covering materials [84].

The following equation can be used to compute K if the heat flux density Q traveling through the material between two enclosures with air temperatures T_h and T_c (T_h greater than T_c) is known [69]:

$$K = Q/A(T_h - T_c) \quad (12)$$

3.3.3. Greenhouse Polymer Films with Temperature-Retaining Particles

Silica Filter Films

To synthesize nanocomposites with improved thermal stability, polymer components were mixed with different forms of silica. According to studies, silica is totally flexible, UV-Vis transparent, and infrared radiation-blocking [85]. It is also risk-free. Various silica particle types have been used in polymers to enhance heat retention. Four composites made of silicon oxide/poly, mesoporous silica nanoparticles, low-density polyethylene, and ethylene-co-vinyl acetate are examined in this section.

Silica Aerogel/Poly (Ethylene-Co-Vinyl Acetate)

Research has been done on a silica aerogel and poly (ethylene-co-vinyl acetate) composite [9]. Through the use of melt-mixing, the silica aerogel (SA) was incorporated into the PEVA matrix. EVA was used to increase the films' visibility [9,86]. The SA-PEVA composite's IR retention characteristics were investigated further using an FTIR spectrometer. An FTIR spectrometer found a ten percent SA-PEVA particle-containing IR insulation to be 80.6% effective. The 90% VIS transmittance of the film proved that the SA-PEVA composite could transmit light using a UV-Vis-NIR spectrophotometer [9].

The results show how sensitive the composite was to SA's IR blocking. According to the study [9], the Si–CH_3 bonds that form during the composite's melt-mixing phase give rise to peaks at 1256 and 846 cm^{-1}. The strong and weak peaks at 1090 and 757 cm^{-1} were produced by Si–O–Si vibrations [9]. Their summits converged and ranged in height. According to research, the SA-PEVA film's IR absorption band spans 1300 to 1000 cm^{-1} [9]. This absorption band demonstrates the exceptional heat retention properties of the SA-PEVA material. The aerogel's homogeneous and random pore size distribution between 30 and 60 nm was identified using TEM scanners. Compared to pore size, the visible light spectrum (780–400 nm) was substantially smaller [87]. The optical transmittance is barely affected by SA inclusion [87].

These results show that the SA-PEVA film's superior heat retention and UV-Vis transmission were due to its distinct shape and distribution within PEVA. Data on temperature variations were used to calculate the SA-PEVA layer's thermal conductivity. Good heat insulation capabilities were attained by lowering the thermal conductivity of the SA-PEVA composite to roughly 0.058 W/mK [88].

Poly(Ethylene-Co-Vinyl Acetate)/Mesopore Silica

Mesoporous silica nanoparticles (MSNs) are fillers that trap heat. By encapsulating CdS-ZnS QDs inside MSNs using a reverse microemulsion, QDs@MSNs nanoparticles were synthesized [88]. The modified QDs were then melt-blended with the EVA matrix and MSNs. Thermometric measurements revealed that the QDs@MSNs in these nanocomposites blocked around 70% of the far-infrared light [9]. There was also a 10% decrease in the transmission of visible light. Infrared radiation shielding is provided by the stretchable mesoporous silica/poly (ethylene-co-vinyl acetate) composite film.

QDs@MSNs/EVA nanocomposite infrared absorption was formed by chemical bonding, just like SA-PEVA nanocomposite. The FTIR spectra of the composite showed a high peak at 1064 cm^{-1} and a less significant peak at 804 cm^{-1} as a result of Si–O–Si vibrations in QDs@MSNs [89]. A peak at 960 cm^{-1} was missed because of Si–OH vibrations brought on by the silanol structure on the silica surface [90]. As seen in [9], QDs@MSNs showed unexpectedly stronger vibrations than SA. These peaks together formed a potent FTIR absorption band between 700 and 1400 cm^{-1}. This band shows how much infrared light an object has absorbed. The mesoporous pore size and surface area of MSNs are both significant (3.80 nm and 650–950 m^2/g, respectively), according to the BET analysis [91,92]. SEM analysis showed that the nanocomposites contained both QDs@MSNs and MSNs. It was assumed that the QDs@MSNs combination had poor heat conductivity based on earlier results [93,94]. Thermal conductivity data provided by the researchers backed up their findings [95]. According to the study, the QDs@MSNs nanoparticles reduced the thermal conductivity of the QDs@MSNs/EVA nanocomposite film by 0.1 W/mK. QD incorporation showed no impact on VIS transmittance, not even with core sizes of 10 nm [95].

Unexpectedly, these QDs enhanced the UV protection of EVA film [95]. By including MSNs as fillers, quantum dot quantum yield and photostability were enhanced [88]. These characteristics make nanocomposite QDs@MSNs-EVA an excellent substitute for greenhouse film [88].

Poly(P-Phenylene Vinylene)/Sol-Gel

Polyphenyl vinyl acetate (PPV) and tetramethyl orthosilicate (TMOS) were combined in a solvent to generate PPV/sol-gel composite [96]. The results show that Poly(PPV)/sol-gel composite film blocks around 70% of the FIR. In contrast, only a fraction of visible light is lost t [7]. Sol-gel/poly (p-phenylene vinylene) can act as an efficient barrier against infrared heat without negatively impacting plants.

The silica network exhibits an absorption band between 1250 and 870 cm^{-1} on the FTIR spectrum. It has been demonstrated that this frequency band effectively filters infrared light [7]. PPV/sol-gel fusion could thereby reduce excessive heat loss. Due to its low VIS absorption and strong UV blocking capabilities, the PPV/sol-gel composite film material demonstrated promise as a greenhouse film material in the UV and VIS bands.

Oxide of Polysiloxane (LLDPE, LDPE, or EBA)

Particles of silicon oxide (SiOx), silica acid (SA), and micro-silica nanocrystals (MSN) can all be employed as insulating fillers in polymers. Research [97] has been done on low-density polyethylene, ethylene butyl acrylate copolymer, and linear low-density polyethylene. This nanocomposite was synthesized by combining a polymer matrix and a SiOx filler [97]. A twin-screw, co-rotating extruder using melt-mixing, SiOx and polymer was used to achieve effective IR blocking. SiOx composite films composed of three different polymer matrices transmit a decent quantity of visible light despite blocking 80% of the FIR. LLDPE, LDPE, and EBA are good infrared heat insulators because of their silicon oxide and polymer components.

IR efficiency can be used to calculate FIR transmittance. Equation (13) shows the *IR* efficiency by comparing the A_{100} and sub-7–13 μm *IR* transmission spectra of the tested film with and without SiOx nanoparticles. Because SiOx nanoparticles naturally absorb *IR*, the average *IR* efficiency was 80%. The mechanical characteristics of the material, such as tensile strength and elongation, were unaffected by SiOx. Therefore, silicon oxide is a good material for greenhouse heat retention.

$$IR_{eff} = \frac{A_{100} - A_1}{A_{100}} \times 100\% \tag{13}$$

The aforementioned heat retention film materials use the *IR* absorption bands as the FIR blocking mechanism based on the idea of vibrational phonon modes produced by atomic bonding. Silica may absorb FIR between 1000 and 750 cm^{-1}, according to interactions between SiO and Si–Si. The composite's capacity to thwart FIR will improve using these exact atomic bonds.

3.3.4. Film Filler Based on Zinc Oxide Nanoparticles

Recent studies [98] have demonstrated that zinc oxide can considerably change the infrared radiation absorption spectra of composite materials (such as polylactide, polyaniline, and LDPE) due to the strong connection between the zinc oxide surface and the polymer matrix. Zinc oxide nanopowder is frequently used to stabilize polymers and polymer composites [99].

A composite's capacity to block infrared light is correlated with the composite's proportion of zinc oxide particles. Numerous composite materials can now more effectively filter infrared radiation thanks to nanoparticles. The ability of polymer nanocomposites to retain heat was improved by adding zinc oxide nanopowders to a polymer matrix. LDPE/ZnO composites, Polyaniline/ZnO Nanocomposites, and Polylactide/ZnO nanocomposites are all covered in this area.

Polylactide and Zinc Oxide

In a study by [100], "inorganic–organic consecutive layer coating" and a high-gravity reactive precipitation process were used to form a PLA/ZnO nano-composite. In a modification tank and RPB, zinc oxide nano-dispersions were handled. The inclusion of ZnO increased the thin film's capacity to block infrared radiation by around 30% without impairing its capacity to transmit visible light. UT-ZnO, or zinc oxide nanoparticles that have undergone RPB processing, can be used in place of T-ZnO to improve the thermal insulation properties of the composite film without compromising its optical light transmission [101]. Using previously described techniques, organic and inorganic coatings were applied to T-ZnO nanoparticles [100,102]. Finally, PLA/ZnO nanocomposites were synthesized via solution mixing. The zinc oxide nanoparticles in the PLA/Zinc oxide nanocomposite film produced a significant transmittance valley between 1450 and 1000 cm^{-1} in the FTIR spectra after 72 h of UV exposure. The relative resistance of the nanocomposites to UV-catalytic degradation was shown by the relative stability of visible bands at 3500 and 1630 cm^{-1} over time [103]. These characteristics help to explain the PLA/zinc oxide composite's outstanding IR performance at the nanoscale. The zinc oxide particles were consistently distributed throughout the PLA, resulting in a higher VIS transmittance than the PLA/UT-ZnO nanocomposites, as shown by TEM images of the PLA/Zinc oxide nano-composite film. UV-VIS spectra showed that the VIS transmittance of the nanocomposites was equivalent to PLA.

Moreover, efficient heat-insulating nanocomposites can be synthesized by mixing zinc oxide and Cs_xWO_3 nanoparticles. CWO was dissolved in butyl acetate (BA), and 50 °C rotating evaporation produced dichloromethane (DCM). The CWO DCM was dehydrated for 12 h at 60 °C under a vacuum to eliminate BA entirely. Before creating ZnO/B-CWO DCM nanodispersions, CWO DCM dispersion and ZnO DCM dispersion were combined for an hour. Between 1000 and 2500 nm, the polylactic acid, zinc oxide, and cadmium WO_3 composite material B-CWO filters around 90% of infrared light [104–106].

Researchers [100] created a heat insulation tester to assess the thermal conductivity of the PLA/ZnO/B-CWO composite. For inspection, the tester was placed atop the glass. An infrared lamp illuminated the glass being tested, and a temperature sensor was placed beneath it to measure the temperature of the component. In the first experiment, glass that had not been treated or coated was used. To test the thermal stability of the PLA polymer, a PLA-only film was used instead of the PLA/Zinc oxide/B-CWO film. Polylactic acid, zinc oxide, and Cs_xWO_3 have outstanding heat-insulating properties due to their higher IR-blocking capacity and slower rate of temperature increase.

Zinc Oxide with Polyaniline

The PANi/ZnO nanocomposites performed very well as an insulating layer [104]. PANi/ZnO nanocomposites were synthesized by mixing ammonium persulfate and zinc oxide dispersion at low temperatures [105]. The PANi/zinc oxide composite material has a negligibly reduced visible light transmission but has an increased FIR blocking capacity of about 30%. PANi/ZnO composite film can now be used as a thermal insulation film for infrared light.

Transmission drastically decreased in the FTIR range. The FIR transmission of PANi/ZnO nanocomposites is around 30% lower than that of PANi alone. The Anderson localization [100], which is covered in more detail at the end of this section, is most likely what brought this about. Across the spectrum, VIS absorption did not significantly increase. The optical properties of the PANi/ZnO nanocomposite layer make it a potent heat insulator.

Zinc Oxide-Based Polymer

Zinc oxide and LDPE were used to build the greenhouse's thermal insulating layer. Blown film extrusion was used by researchers [107] to make an LDPE/zinc oxide composite. The spectrometer showed that the IR insulation efficacy of the LDPE/zinc oxide composite rose from 39% to 44%. As a result, the LDPE/ZnO composite film's infrared thermal insulation properties have been enhanced.

We conclude that this occurrence was significantly influenced by Anderson's localization [99]. The LDPE/ZnO composite effectively blocked UV light without compromising

VIS transmission, as shown by the UV-Vis spectra [106]. Two distinct mineral oxides with micrometric widths, cerium, and titania may improve the effectiveness of thermal insulation in films.

3.3.5. Greenhouses Agro-Photovoltaics (PVs)

The development of sustainable materials for use in agriculture has been the subject of numerous studies, including those on biodegradable polymers made from agricultural waste, sensors to check on the health of silos and other agricultural structures, and sustainable materials for greenhouse coverings. Solar greenhouse covers, which can control the microclimate inside greenhouses, reduce carbon emissions, and generate electricity, have not received enough attention, though. Solar energy systems can annually reduce carbon emissions by 1735 kg. Using greenhouse covering materials may reduce carbon footprint, depending on how well the current material constraints are resolved.

Three different categories—shared structure, sunshine systems shared structures, and nearby—can be used to categorize the integration of PV modules into greenhouse constructions. The headhouse and the storage facility are neighboring structures of the adjacent category and are fixed with PV systems. The nearby configuration of PV modules and greenhouse buildings is viewed as less suitable, given the necessity of optimizing land allocation and careful resource management in commercial farming. Building-integrated photovoltaics (BIPVs) reinforce the argument for shared configurations. The current research focuses on developing greenhouse PV modules and centers primarily on covering materials.

The benefits of current PV materials are the basis for the need to develop new materials, and there are a variety of solar greenhouse designs. Numerous advantages and disadvantages of PV systems have been noted over time. PVs, for instance, can create the ideal environment for plant growth without the use of machinery or outside energy sources. However, PVs also showed disadvantages, such as a reduced ability to hold onto soil heat and optimal sunlight accumulation on the northern wall, which led to significant heat fluxes and increased the need for active heating to regulate the soil and air temperatures inside for the more pronounced plant growth. Various issues surround the cost of commercially available electrochromic glass or liquid crystals distributed in polymers. Researchers have shown that the energy flows in a greenhouse could forecast the need for heating and cooling. The physical components of a greenhouse, such as the soil, plants, and water, as well as the surroundings, impact the energy flows (see Figure 1). In a greenhouse, several processes, such as air exchange, plant transpiration, heat transfer, and heat conduction, depend on controlling the microclimate.

Commercial greenhouse energy requirements could be cut using PV-based energy to regulate the indoor microclimate. Additionally, this would result in lower running costs for artificial lighting. The interior greenhouse environment, according to research, was principally controlled by energy from various sources, and semi-transparent BIPV. They also considerably affected the production of clean energy in the area of use.

Semi-Transparent PV Greenhouses Covering Materials

- Graphene- and Fullerene-Based Greenhouse Covering Materials

The development of carbon allotrope-based materials, such as fullerenes [108], carbon nanotubes (CNTs) [109–112], and graphene [113], will define the greenhouse properties of the future. Pb-based QDs are susceptible to performance loss, surface oxidation, environmental deterioration, and low stability. These issues show how dependable technology is. Increased UV exposure makes the issue worse.

The quantum yield of photoluminescence (PL) in graphene-based QDs was enhanced to 65% by significantly lowering reabsorption losses [113]. For dual-controlled glasses [114], researchers [113] have synthesized thermotropic hydrogel–graphene oxide molecules with auto-adjustable transparency. The graphene oxide turned solar energy into heat, which prevented it from reaching a structure. The glass's transparency was converted to opacity during the conversion process, which decreased its capacity to absorb solar energy.

Although graphene-based devices offer superior optical and electrical features, scaling up graphene synthesis remains difficult [115–118]. It will be very challenging to produce compounds with graphene as an additive.

Focusing on fullerene-based materials for greenhouse covers makes sense because they can be made inexpensively and without restrictions. A carbon allotrope that resembles graphite called fullerene is well suited for enhancing power conversion efficiency (PCE) in PV materials [119]. This is made possible, among other things, by the scalable chemical conjugation, huge HOMO-LUMO band gap, and low reorganization energy of fullerenes [119]. The optimal fullerene ratios for charge extraction, open-circuit voltage, and trap-assisted recombination must be determined. The usefulness of products made from fullerene may also be questioned, given the gradual transfer of research and development achievements to the commercial sector. One element contributing to the current problems may be the inadequate translation of advances.

The study on polymer fullerenes by [119] served as the foundation for the initial investigation into these substances. Modular photocurrent-generating devices based on fullerene and phospholipids were being researched at the time [120]. Since then, it has been found that phospholipid-derived amphiphilic C^{60} derivatives are excellent for incorporating fullerenes into modules. In addition to photo-induced charge conversion and HOMO-LUMO charge conversion, this approach also permits the transfer of electrons and energy.

Fullerenes were identified as a useful material in the aforementioned studies [119–121] because of their affinity for electrons and capacity for charge transfer. According to the research, polymer fullerene is now the most efficient chemical. Although exciting results from recent research on practical synthesis techniques for chemicals based on fullerene have been found, these concepts have not yet been put into practice [122]. The substance's hydrophobicity is a flaw. One of the subjects discussed was the challenges brought on by the commercialization of fullerene.

It is possible to get around the limitations of current materials such as chlorophyll in plants by spectrally modifying the absorbance spectrum of the modules to achieve optimal light harvesting (PAR transmittance) and by coordinating the transmission spectra of the ST devices with the absorption spectra of the photoreceptors (chlorophyll in plants). Crop quality and yield can both be increased by changing the PAR [123]. Increases in spectral characteristics might boost solar energy absorption and photosynthesis. Despite being designed to prevent sunlight, greenhouses contain materials that react differently in terms of PCE, quantum efficiency, and plant growth factor [124]. No new greenhouse construction materials will be commercially certified until the PAR issue is resolved.

- Phase-Change Materials

Compounds known as phase-change materials (PCMs) absorb and release thermal energy as they change phase (known as latent heat). When a substance melts, it changes from a solid to a liquid form. During the phase change, several materials have the ability to absorb a significant amount of heat energy. PCM employs passive heating to warm the greenhouse by fusing latent heat. In other words, these materials naturally collect solar energy during the day and release it at night, keeping the greenhouse significantly warmer on chilly winter evenings (for further reading, see [125–130]).

Because greenhouses are designed to capture as much solar energy as possible for photosynthesis, it is difficult to retain excess heat. Excess heat can be effectively dealt with by storing thermal energy in a greenhouse with solar collectors, phase-change materials, heat-storage and heat-release devices, and geothermal energy [131]. Growing plants are sensitive to changes in humidity and temperature, and greenhouses can only take so much heat. To recover waste heat, greenhouse technology frequently employs PCMs [132]. Effective thermal energy storage is possible with these materials. The study by [132] found that using PCM plate containers cut greenhouse gas emissions by 23.7% and gave a four-month payback. Similarly, a second study by [133] found that installing PCM caused a temperature drop of up to 3.7 degrees Celsius in a greenhouse case study where PCM material was not used. Additionally, they showed that while the PCM was operating, the inside temperature remained constant at 10 degrees Celsius. The study by [133] also reported that the use of PCM in greenhouse walls raises the interior temperature, soil temperature, and outside temperature. It has been shown in numerous investigations that PCM has an impact on greenhouse interior temperatures. The ideal greenhouse covering materials for temperature changes between 25 and 52 degrees Celsius will be determined using energy modeling and the adoption rate of phase change materials [134]. Polymers, hybrids, and alloys with shape memory as examples of phase-change materials are demonstrated by [135–137]. In the second scenario, shape-memory effects brought on by solar radiation might enable PCMs to control greenhouse air quality more effectively. It is possible to synthesize new morphological modifications by utilizing hydrogels' hydrophilic and water-absorbent properties.

Before the materials may be used for larger applications, surface defects must be eliminated. Cost issues are also a result of PCMs' higher prices than traditional materials [138]. The results of another research study by [139] agree with those provided by [138]. Another time, it was said that the high price of PCMs was due to their expensive integration with other parts, specifically HVACs. Incorporating HVAC systems in greenhouse projects may not be economically feasible.

By developing morphing building skins for buildings and other structures like greenhouses, HVAC expenses can be cut to a certain level [136]. Using photovoltaic systems to transfer power to regulate or activate the shape-changing materials could boost the efficiency of the buildings. Because they are not commercially viable, PV-shaped morphing materials cannot be used to replace HVAC systems in greenhouse constructions. Numerous physical (peak/horizontal global sun radiation, direction, weather, sunlight penetration depth, etc.) and physiological factors, including those listed in [136], can affect the behavior of shape-morphing materials. It may be tough to adjust any of the aforementioned qualities for usage as greenhouse claddings.

It is crucial to determine whether self-aligning modules can be used since there are no solutions to these problems in the real world. The pilot research findings by [133] support the concept's applicability and realism, with the exception of the search algorithm's criteria. The widespread use of shape-shifting skins in commercial greenhouses is constrained by the addition of search algorithms, which increases capital costs. Another study by [140] suggests that by making PCMs more sensitive to sugars and other biomolecules, CO2, mechanical stress, pH, and temperature, the advantages of PCMs may be increased. A possible strategy could be the use of transparent modules arranged in a chevron pattern [141]. It was obvious that additional materials, specifically LSCs, were needed because PCMs have particular requirements.

- Luminescent Solar Concentrators

Due to technological advancements, absorption and photoluminescence could increase the economic viability of dye lanthanide complexes, colloid nanocrystals, and Stokes shift-customized nanocrystals (see Figure 4) [142]. Due to a number of problems, LSC materials cannot be used in a commercial setting. Copper-doped InP/ZnSe quantum dots for luminescent solar concentrators have low PCE and EQE values (3.4% and 5.9%, respectively) since it has historically been difficult to synthesize large quantities of LSC materials/chromophores with certain material properties [143,144]. For chromophores of types A and B, it is necessary to modify the optical absorption spectrum and absorption coefficient. The spectral coverage of PbS is more extensive than that of $[Eu(TTA)_3(TTPO)_2]$ and 4-dicyanomethyl-6-dimethylaminostiryl-4H-pyran (DCM) [144]. Recent discoveries and developments have bolstered the area of LSCs, with most of the major design and synthesis challenges now effectively resolved.

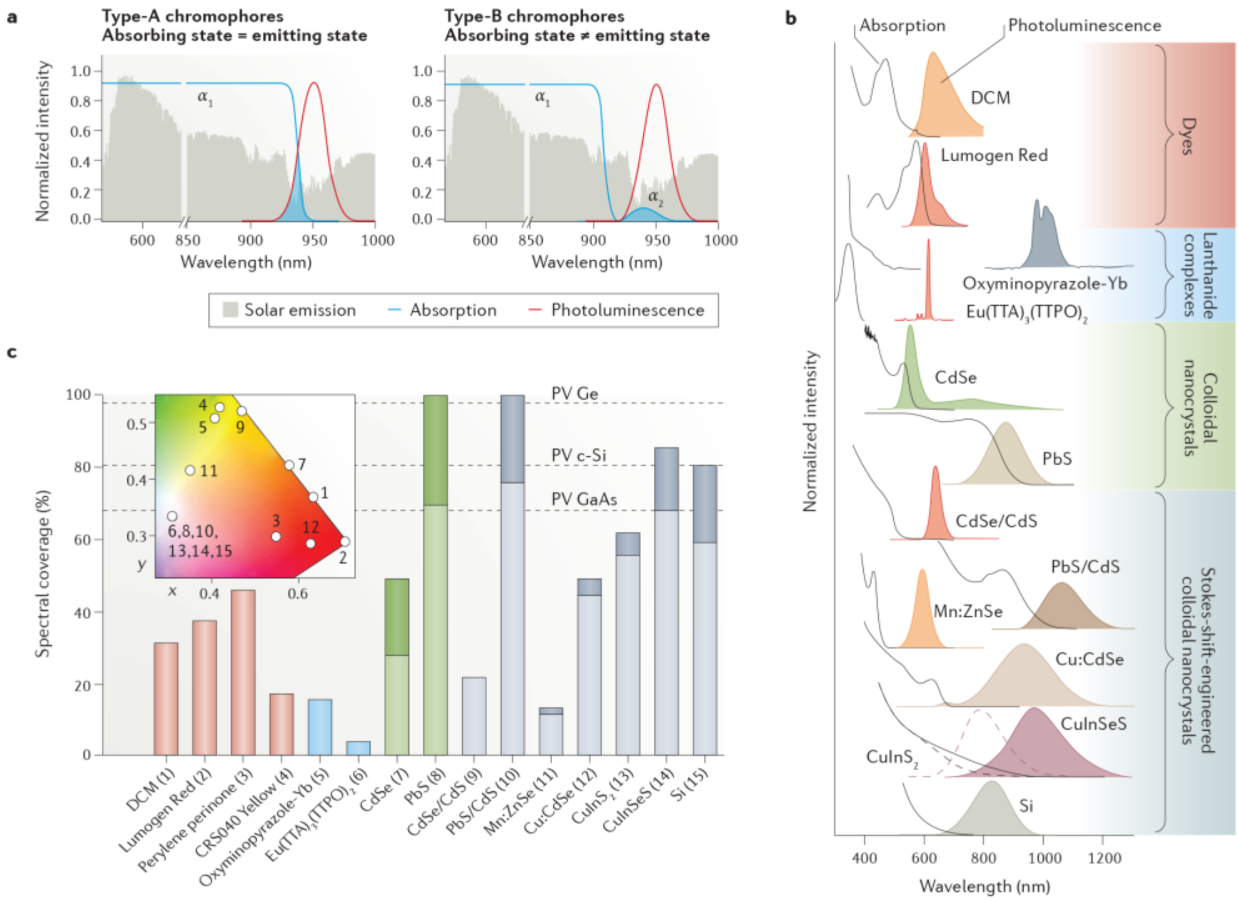

Figure 4. (**a**): Absorbance and emission state; (**b**) normalized intensity; (**c**) spectral coverage percentage [142].

4. Environmental Sustainability of Greenhouse Covering Materials

Recycling is crucial because it lessens the waste generated during the production of glass, films and sheets made of petroleum, and agricultural activities. In Europe, 0.61 million additional tons of trash are produced annually [61]. PVC and other polymers are in higher demand than ever, particularly in Western Europe. The demand for plastics increased by a factor of six between 1960 and 2004 [64], according to the European Commission. The characteristics of plastics that make them popular, such as low energy consumption during production, recyclability, UV resistance, adaptability, and affordability, are directly influenced by market demand. Recycling is still the best option because there is no practical way to completely reduce the demand for PVC.

4.1. Mechanical and Chemical Recycling

Recycling has a substantial carbon impact; thus, continuing to use plastics will negatively influence the environment, as shown in Table 1. The estimated carbon emissions were computed based on life-cycle analysis and global norms. Theoretically and empirically, paper has the largest emissions, but low-density polyethylene has the lowest (29 kg CO_2 e/t). Moreover, 395 kg CO_2 e/t of carbon dioxide is produced while recycling various types of glass. Recycling polyethylene terephthalate and low-density polyethylene is more advantageous for the environment than recycling high-density polyethylene, paper, wood, and glass.

Table 1. The carbon footprint associated with the recycling of selected greenhouse covering materials [145].

Waste Material Type	Calculated Emission Factor		Literature Emission Factors		
	Gross $kgCO_2e/t$	Net $kgCO_2e/t$	No. of Reference Studies	Range $kgCO_2e/t$	Average ± St. Dev. $kgCO_2e/t$
Green glass	395	−314	6	−762 to −201	−417 ± 176
Brown glass	395	−314	6	−762 to −201	−417 ± 176
Clear glass	395	−314	6	−762 to −201	−417 ± 176
Mixed glass	395	−314	6	−762 to −201	−417 ± 176
Paper	1576	−459	7	−3891 to 390	−1195 ± 1303
Mixed plastics	339	−1024	6	−2324 to 1470	−788 ± 1007
Mixed plastic bottles	336	−1084	5	−2324 to 1470	−922 ± 1321
Polyethylene terephthalate	155	−2192	6	−2324 to −566	−1570 ± 600
High-density polyethylene	379	−1149	5	−2324 to −253	−1055 ± 792
Polyvinyl chloride	379	−1549	3	−2324 to −566	−1259 ± 936
Low-density polyethylene	29	−972	4	−1586 to −850	−744 ± 981
Polypropylene	379	−1184	3	−2324 to −566	−1279 ± 925
Wood	502	−444	5	−2712 to 1	−619 ± 882
Chipboard & MDF	502	−444	5	−2723 to 1	−620 ± 886
Composite wood materials	502	−444	3	−1266 to 1	−357 ± 431
Soil	41	27	2	−2 to 2	0 ± 2
Plasterboard	59	4	2	−139 to 33	−53 ± 122
Paint	364	86	1	–	−2840

Mechanical methods are the most efficient for recycling polyethylene, polyvinyl chloride, ethyl vinyl acetate, and other polymer products, according to a study by [146]. However, plastic additives make producing virgin polymers through recycling more challenging [54]. Due to chemical heterogeneity and other undesirable traits, such as low optical quality, the value of recovered polymers has decreased. Different techniques can be used to recycle greenhouse cover materials, depending on how many cross-links are present. Due to the deterioration and subsequent loss of the original polymer structure, mechanical recycling is not practical [147]. Stabilizers and additives, however, cannot reverse the process.

Mechanical recycling is better than landfilling or turning plastic trash into synthetic fertilizer, notwithstanding the drawbacks of current recycling techniques [148,149]. Considering how much is produced each year, it can be difficult to eliminate agricultural plastic waste in landfills [148,149]. The adoption supports the hypothesis that vinyl ester, UPE, and diol synthesis and oxidation lead to the formation of virgin cross-links (Figure 5).

Plastics must be mechanically separated from objects and recycled like regular plastics. Therefore, it is not advantageous to recycle plastic waste to produce concrete-like wall and flooring materials [59]. The physical recycling of PVC greenhouse parts could result in the release of the aforementioned heavy metal stabilizers into the environment. Before using chemical recycling, the mechanical recycling limits are considered. PVC plastic waste needs to be combined with other materials that contain less PVC in order to be chemically recycled [59]. The only drawback is the lack of reliable chemical recycling options.

Prior recycling is necessary because polymers cannot be mechanically recycled without separation. As a result, it is not possible to create walls and floors made of plastic trash that resemble concrete [64]. The previously mentioned heavy metal stabilizers may be released into the environment during the mechanical recycling of PVC greenhouse materials. Mechanical recycling restrictions are taken into account while thinking about chemical recycling. PVC plastic waste is mixed with compounds that rarely or never contain PVC during the chemical recycling of polymers [64]. The lack of a solid infrastructure is the only obstacle to chemical recycling.

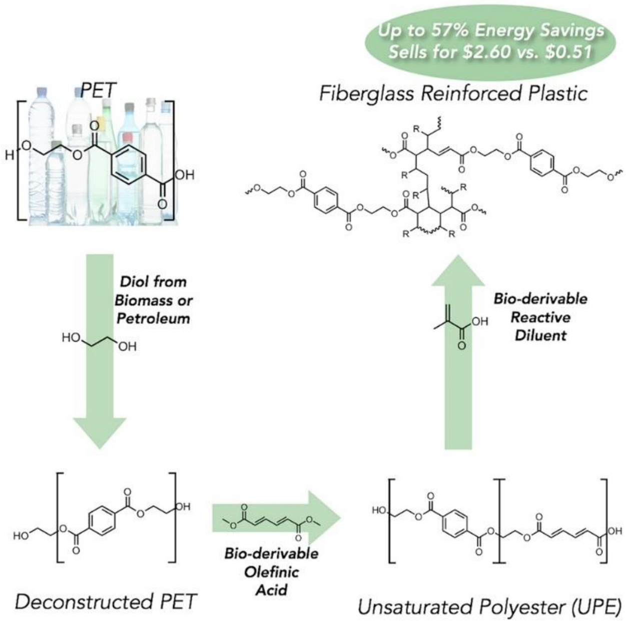

Figure 5. High-value fiberglass reinforced plastics from low-value PET via UPE synthesis [146].

4.2. Closed-Loop Recycling

Discarded plastics and plastic films can be recycled in closed-loop systems to synthesize post-consumer plastic films used in greenhouses. Closed-loop recycling technologies create post-consumer materials with nearly identical qualities to virgin plastics (Figure 6), as opposed to using mechanical and chemical recycling to create cement substitutes [67]. The restriction is pointless because the agricultural industry is responsible for 30% of greenhouse gas emissions [150,151]. The smaller peaks at 1450 cm^{-1} and 1700 cm^{-1} denote C–H bends and C=O bonds, whereas the more prominent peak at 2950 cm^{-1} shows C–H stretching [152]. The possibility of oxidative damage from oxygen species in carbonyl groups can be decreased through phytostabilization. It is possible to mix mono-polymers to address minuscule alterations in molecular structure.

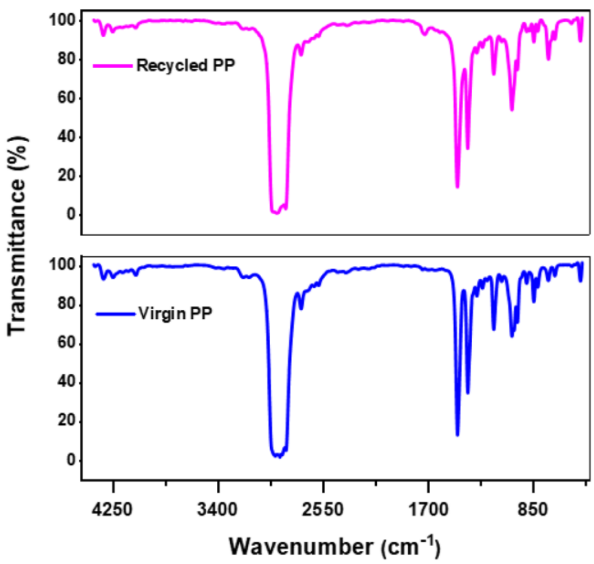

Figure 6. FTIR spectra of recycled vs. virgin plastics [153].

Reprocessing, molecular structure reconstruction, mixing, thermomechanical, micro-twin-screw extrusion, commercial ethylene-glycidyl methacrylate synthesis, and radical generator activities are all examples of closed-loop recycling operations [147]. Polymers are synthesized when polyethylene is melted and photo-oxidized to reconstruct its molecular structure, which causes branching and cross-linking. Future studies should concentrate on this issue because biofilm development and dust accumulation on greenhouse cladding materials have been proven to reduce recycling. Carbonyl groups represent the only substantial restriction because they raise the possibility of photooxidative damage. Recycling maintains the degraded molecules' chemical structure while also lowering carbon emissions.

Tinuvin 327, Sandostab P-EPQ (P-EPQ), and light stabilizers are used to photo-stabilize PF (or recovered polymers from abandoned greenhouse materials) in order to prevent photodegradation and weathering [154]. The best outcomes have been seen between 1500 and 1700 h, despite stabilizers needing to be present in a concentration of about 2500 ppm in order to be effective [154]. The process improves the durability of LDPE, LLDPE, and EVA plastics and films in addition to other polymer materials. Researchers have claimed that stabilizing agents were used to enhance the performance of materials prior to extrusion [154]. As shown in Figure 7, the most significant increase in tensile strength was in the PF polymers, including antioxidants and UV absorbers. The stabilization method also encouraged dimensionless elongation.

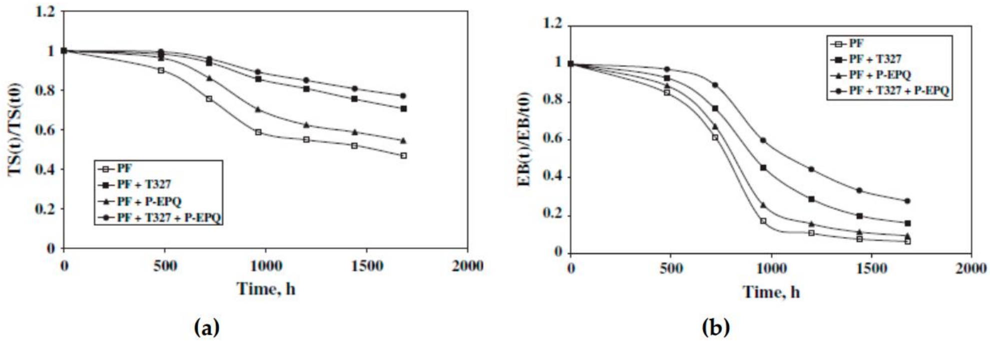

Figure 7. Photo-stabilized and unstable PF plastics: (**a**) Tensile strength and (**b**) dimensionless elongation [155].

4.3. Bio-Based Polymers Synthesis

The production of bio-based polycarbonates, which can be used as components of greenhouse cover materials, is now made simpler and more environmentally beneficial thanks to the synthesis of polymers from the renewable feedstock or the coupling of carbon dioxide. Figure 8 shows that fatty acid chains and commercial or agricultural monomers are among the initial components [156]. Only the types of functional groups, the degree of cross-linking, and the optical and mechanical properties of polymers that can be made from various biomass sources are subject to these restrictions.

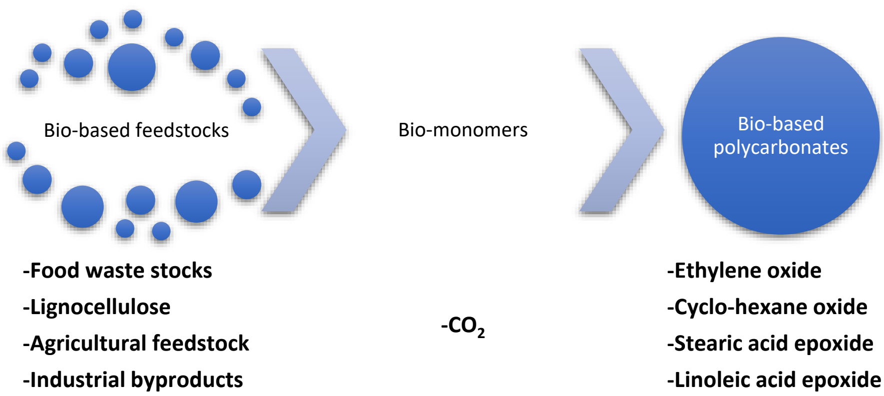

Figure 8. Synthesis of bio-based polymers [155].

Closed-loop systems and bio-based products cannot fully minimize the carbon footprint because industrial facilities emit greenhouse gases, including nitrous oxide, carbon dioxide, and methane [154,157]. Due to upcycling, greenhouse materials are becoming more environmentally friendly.

5. Discussion

In order to maintain the light levels required for crop growth, development, and production (for example, infrared light transmittance in summer), the high-energy wavelengths that enter the greenhouse during the day should be reduced by a cover material. It must also be designed to prevent long-wavelength heat loss at night. When there is insufficient light, it is thought that the quality of the light, specifically the proportion of blue and red light, is essential for photosynthesis [158]. In vertical culture, a well-designed cover material may promote the best vegetative and reproductive growth, particularly on the sidewalls (raising red and far-red light) and roof (balancing blue and red light). It may be necessary to select a balanced seasonal light environment for the year-round production of both the short-growing season crops (1–2 months, like lettuce) and the long-growing season crops (8–12 months), like tomato capsicum and eggplant [159].

The world's population and income are growing, and customers are demanding more and better fruits and vegetables without having access to more land to grow them on; thus, it is evident that the productivity of the greenhouses must increase. The knowledge of how different types of light affect plant growth is growing. The majority of the static materials that have been utilized to study lighting requirements cannot change the lighting on an hourly or even daily basis. It is clear that much more research needs to be done on cutting-edge optical materials developed expressly to manage sunlight for use in greenhouse structures. This analysis clearly demonstrates that research on covering materials could, with the appropriate adjustments, have a considerable future impact on greenhouses. To understand how these devices affect crop development, larger-scale synthesis and testing are required.

In order to meet the demands of this expanding industry, this study emphasizes the challenges the horticulture sector faces and the need for flexible optical materials and equipment. The unproven photo-stability of the materials may be the biggest barrier to the widespread use of responsive materials, possibly even surpassing price increases. Several liquid crystals, polymers, and dyes that have been proven to deteriorate in the presence of UV radiation are discussed in this study. Crop farmers need these covering materials to have longer lifespans before they even seriously contemplate employing them. Moreover, the use of innovative coverings that do not quickly turn translucent is resisted by farmers. It is crucial to keep in mind that if the overall light transmission is unaffected, diffusiveness might be advantageous. In addition to the hemisphere's total light transmission level, there are other variables. Future studies in this area will put much emphasis on finding answers to these issues.

Furthermore, in order to improve vegetable nutrition and advance crop production knowledge, it is critical to conduct thorough molecular research on how cover materials affect greenhouse climate. Furthermore, because crop quality accumulates during manufacturing, influencing product quality and shelf life, it is critical to consider how cover materials affect plant development. To make use of the improved energy-saving cover materials, more research should be conducted on the network of photosynthesis, yield generation, and nutrient accumulation controlled by light. This will demonstrate how important cover materials are for growing vegetables in greenhouses. Researchers will employ the right cover materials to enable more sustainable covered cropping. These researchers have training in plant physiology, molecular biology, chemistry, materials science, photonics, and greenhouse horticulture (Figure 9). This will probably increase greenhouse vegetable productivity and quality for greater human health and lower the carbon footprint of horticulture agriculture.

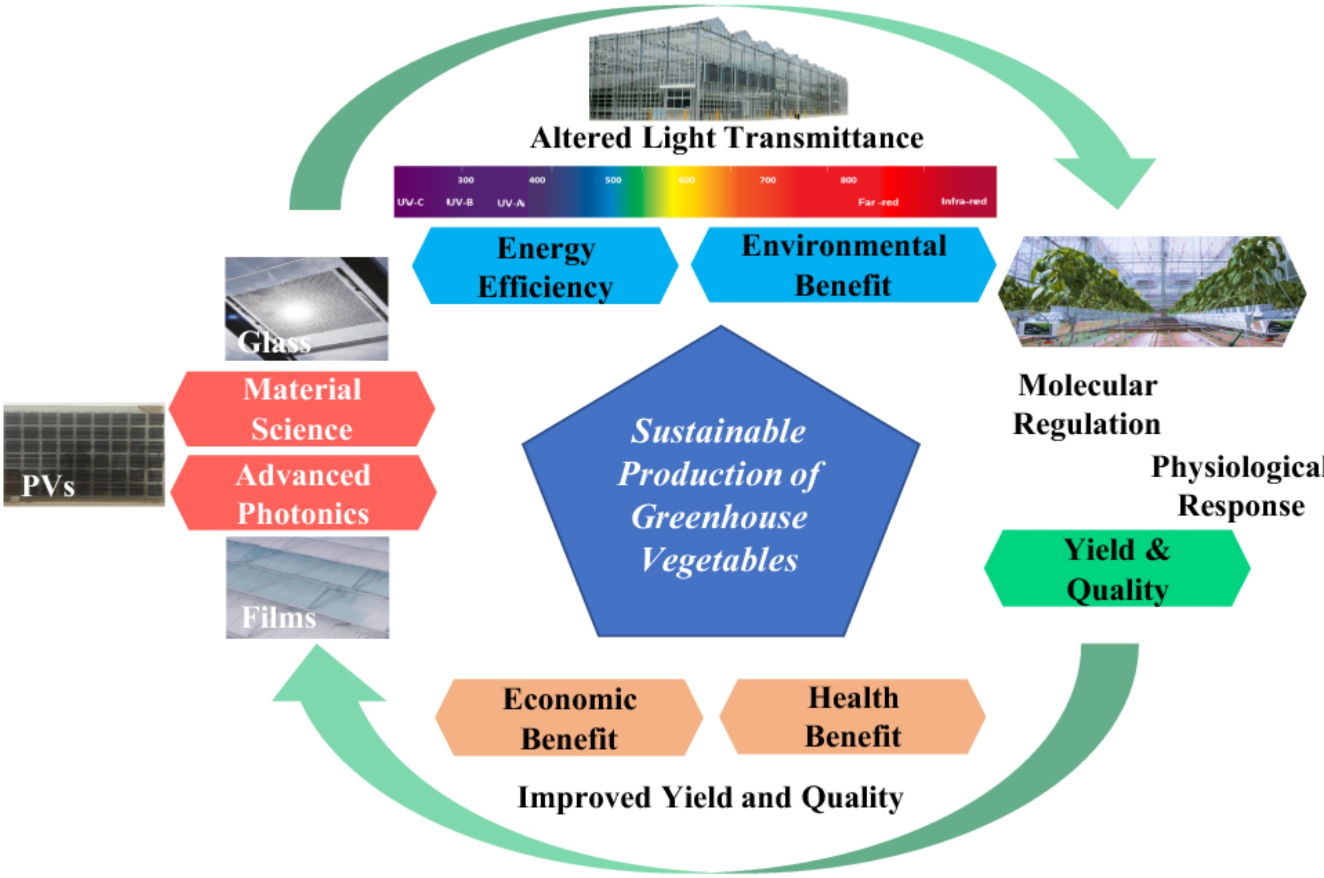

Figure 9. The link between sustainable horticulture production and cover materials [159].

6. Future Outlook and Perspectives

The pace of research and development, the commercialization of modern technologies, and the cost–benefit evaluation of novel materials will all have an impact on the future prospects for greenhouse coverings. In order to address the many challenges researchers are currently confronting, such as the diverging PCE of different materials, it is imperative to produce novel greenhouse covering materials constructed of modules with the maximum PCE and plant conversion factor. The industry's natural search for novel materials is encouraged by the financial advantages of existing materials.

Organic materials that are semi-transparent have a greater PCE than Cu_2O films (17% and 10%) [160]. However, the PCE of 7.7% for semi-transparent polymer materials contradicts this [119]. The statistics show that the advantages of PCE are not always obvious when switching from metal oxides to organic molecules. Several strategies exist to overcome the constraints due to plant growth factors, including the use of fullerenes, creative quaternary pairings, and ecologically friendly green synthesis [161]. Fullerene-based materials, PCMs, and energy modeling are being studied more frequently in the context of greenhouse coverings due to their viability and potential to overcome the limits of current materials. The cost–benefits of PCMs, fullerenes, and other materials are presented in Table 2 [138]. According to a comparative study, the three main barriers to adopting new materials are cost, environmental sensitivity, and environmental impact.

Table 2. Cost–benefits of materials for greenhouse covers [138].

Name of Smart Material	Advantages	Disadvantage
Piezoelectric materials	High sensitivity and stability	Not used for static measurements
Magnetostrictive materials	High energy density, Intrinsic robustness	The intricacy of material gets increased. Enough experimental evidence was not found
Rheological materials	Application of electric or magnetic field changes its physical state	Not easily available to work with
Thermo-responsive materials	Change physical property when exposed to temperature variation	Costly
Electrochromic materials	Change of optical properties when an electric current is passed	low coloration efficiency and durability
Fullerenes	Highly stable, versatile in nature	health and environmental impacts
Biomimetic materials	Strength, camouflage, waterproofing	Poor abrasion resistance, sensitivity to moisture
Graphite Fibers	Excellent tensile strength, low coefficient of thermal expansion	Break when compressed, machining weakens the GF
Transparent Aluminum	High strength	Minimizing impurities, eliminating micropores, controlling grain boundaries
Transparent concrete	Transmit light effectively, environment friendly	High initial cost, casting is difficult
Self-healing coating	Self-healing, reconstruct and repair itself	High-viscosity resin should not be used, time-consuming
Shape memory metals	Elastic in nature, high strength	Costly to machine and manufacture
Aerogels	Efficient and adaptable highly porous solid or semisolid materials used in place of insulation	Clarity is low, reduced surface area
Self-sensing concrete	Detect a small change in strain and stress	Inability to detect early stage of damage
Smart bricks	Detect stress, sound levels, chemical changes, moisture content, types of forces and vibration.	Issues of maintenance and durability, expensive.
Smart wrap	High strength	Technology is in the initial stage
	Temperature control	
Smart Glass	Modify the amount of light and heat, cost-effective	High initial cost
Phase change material	Absorbs or releases latent heat, saves energy	Costly, compatibility with the material needs to be identified

7. Conclusions

Future advances in nanomaterial synthesis at the micro- and macroscales may make it possible to use more covering materials for greenhouse structures. These developments are essential for addressing the problems of ambient deterioration in Pb-based QDs, surface oxidation, performance loss, and poor stability while minimizing the negative environmental effects. Thanks to nanotechnologies, long-term advances in commercial agriculture management practices are projected, which will be beneficial to humanity. Better greenhouse investments can be made to aid in food production. However, if there is no agreement among important actors, the potential applications of technical solutions for greenhouses may be compromised. The extreme sensitivity of PVs to outside climatic and meteorological variables served as additional evidence in favor of this approach.

Regardless of disagreement, there is undeniable evidence that materials used for greenhouse covers can control the microclimate to reduce CO_2 emissions, limit energy use, and increase crop yields. Similarly, an in-depth examination of the applications of various greenhouse technologies reveals that advancements provide financial benefits, particularly in terms of reduced greenhouse heating and cooling costs. PCMs are a good example of this, as they reduce the greenhouse's operating costs by maintaining consistent ambient temperature levels.

According to the review, using greenhouse covering materials based on solar PV modules offers some special advantages. Numerous PV materials have been created as a result of recent advancements in greenhouse technology, such as BIPV, EG, and PV materials made of Pb-quantum dots, amorphous tungsten oxide films, copper-doped InP/ZnSe QDs, and Pb-free materials. Other PV materials include 2D Ruddlesden, Pb Halide Perovskites, copper-doped InP/ZnSe QDs, and semitransparent solar cells. Additional LSC configurations and luminescent solar concentrators with copper-doped InP/ZnSe QDs were found to be less suitable for greenhouse covering due to their low PCE after evaluating the various material classes. On the other hand, the 17% PCE semi-transparent organic solar cells are. The variations in crop yield, PAR, plant growth factor, cost, durability, and PCE, as well as the ecological impact of materials, i.e., PV Pb-quantum dots, Pb Halide Perovskites, 2D Ruddlesden-Popper perovskite-based solar cells, and amorphous tungsten oxide, underlined the necessity to concentrate on the LSCs since they are crucial to the covering materials' future. Improvements in type A and type B chromophores' absorption coefficients and optical absorption spectra are the reason for this. Beyond LSCs, the desired characteristics can also be found in PCMs and fullerene-based materials.

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