

Pyrolytic Behavior of Photovoltaic Modules

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Abstract. With the rapid development of the photovoltaic industry, many early photovoltaic modules have been reduced in photoelectric conversion efficiency and have entered the end-of-life stage, resulting in a large amount of resource waste. How to realize its resource recovery has become an urgent environmental and technical problem. Although there have been many studies on the recycling of PV devices, they are still industrialized. This is because there is no summarized discourse on the current development. This paper summarizes the structural composition of crystalline silicon photovoltaic modules and the pyrolysis behavior of the main materials, focuses on the decomposition characteristics of EVA encapsulation materials and backsheets under two atmospheres of nitrogen pyrolysis and air combustion, and explores the reaction mechanism, product distribution and synergistic effect in the pyrolysis process. The research progress of the co-pyrolysis strategy in enhancing the resource recovery efficiency and reducing the generation of harmful products is further summarized. This paper provides theoretical references for optimizing the heat treatment parameters and designing green and efficient recycling process, which is of some guiding significance for constructing a low-carbon recycling system of photovoltaic.

Keywords: Photovoltaic module, Nitrogen pyrolysis, Air pyrolysis, Backsheet, Co-pyrolysis

1. Introduction

With the growth of energy demand and the depletion of traditional fossil energy sources, energy transition has become the focus of global attention. Recently, the country has put forward the carbon peak, carbon neutral strategy, clean energy has become an indispensable part of social development. Solar energy and other utilization of photovoltaic power generation technology by virtue of its green, rich resource potential and sustainability has received widespread attention. However, with the rapid development of the photovoltaic industry, many of the early photovoltaic module photoelectric conversion efficiency cliff-style reduction, has entered the end-of-life stage. The service life of PV modules is usually 20 to 25 years, and it is predicted that by 2030, the global disposal of used PV modules will reach about 8 million tons, and by 2050 it will increase to 20 million tons. This makes the recycling of used PV modules an important challenge for the PV industry.

PV modules contain a large number of valuable resources, such as silicon, aluminum, silver, copper and other metal materials, as well as glass, plastic and other non-metallic materials.

Recycling these resources not only reduces environmental pollution, but also reduces the demand for new raw materials and promotes the recycling of resources. However, the imperfect industrial chain, less technical research and high cost have become the constraints to the development of PV recycling technology. At present, the recycling technologies of waste PV modules mainly include mechanical dismantling method, organic solvent method, acid-base method and heat treatment method. This paper summarizes and analyzes the optimization strategy of the above recycling technologies, which is of some guiding significance for the development of the PV recycling industry.

2. Components of photovoltaic modules

Crystalline silicon photovoltaic module is the basic component of photovoltaic power generation system, composed of a variety of materials in conjunction with each other, to ensure the long-term stable operation of the module, in the subsequent material pyrolysis and recycling of materials in the study provides an indispensable material and process basis. The main structure of the module mainly consists of surface glass, EVA adhesive film, silicon-based cell and backside protective film, and these key layers determine the working performance of the PV module [1-2].

The outermost layer of the module is high-strength optical glass, which directly protects the module structure. This type of glass needs to have both excellent mechanical strength and high transmittance, and can resist strong external impacts and damage from the natural environment (e.g., high winds, heavy rain, hail, etc.) without affecting the light transmission [3]; in addition, to further reduce the reflective losses of the incident light on the glass surface, some module designs deposit a functional reflective reduction film on the surface of the glass, which improves the light transmittance and enhances the cell's output power [4].

The various types of structures inside the PV module are bonded and cushioned with each other by the encapsulation medium, and the commonly used encapsulation material is ethylene vinyl acetate copolymer (EVA). It undergoes a temperature cross-linking process during the encapsulation lamination process, which can bond the cell and the upper and lower substrates into a reliable encapsulated whole [5]. The EVA material has a certain degree of elasticity and flexibility, which can absorb a certain amount of stress during transportation and use, reducing the possibility of damage by mechanical loads. At the same time, the optical transparency and electrical insulation of the material also has a certain guarantee. As the material has a tendency to yellow easily with aging, it is also one of the focuses of the current research on recycling and material durability [6].

Silicon-based cells, the most central component of the module, are generally made of monocrystalline or polycrystalline silicon, which is the main layer that absorbs light energy for electrical energy conversion, and internally forms a PN junction through doping to form photogenerated carriers under light irradiation, and then forms an electric current driven by the built-in electric field in the PN junction [7]. Improvement of light absorption is carried out by surface suede and anti-reflective films, as well as by electrode patterning and metallization to influence the electrical output and conversion efficiency [8].

The lowest part of the module is the backsheet material, which serves to prevent water vapor and ultraviolet rays from entering the structure and eroding the internal structure. The backsheet material mostly uses composite polymer film, the main requirements for good thermal stability, insulation and mechanical strength, can meet the long-term outdoor use environment [4]. Not only play a sealing, protection, but also play a certain role in regulating thermal management, to avoid the degradation of material properties caused by high temperature. The aging resistance of the backsheet has been shown to be a major cause of module failure as the usage time increases [5].

From the viewpoint of the above four structural levels, the close coordination and interdependence between the functional layers synergistically realizes the energy conversion performance and structural stability of the PV module. The analysis of the pyrolysis behavior of the material properties of the core layers of PV modules is beneficial to the recycling of PV modules and the low-carbon recyclable development of solar photovoltaic panels.

3. Progress in the study of pyrolysis

In the recycling treatment of waste photovoltaic modules, the pyrolysis behavior of encapsulation materials has a key impact on the efficiency of resource recovery. Among them, EVA adhesive film and backsheet materials (e.g., PET, PVDF, TPT composites), as the main polymer components, show significantly different pyrolysis characteristics under different atmosphere conditions. According to the different atmosphere environments, pyrolysis methods can be mainly categorized into nitrogen pyrolysis and air combustion methods.

3.1. Pyrolytic behavior of EVA adhesive films

3.1.1. Nitrogen pyrolysis

In an inert atmosphere such as nitrogen, the EVA pyrolysis process can effectively avoid oxidative damage to metal electrodes, which is suitable for recycling high-value materials. Farrell et al [6] systematically investigated the pyrolysis process of EVA adhesive film in waste photovoltaic modules under nitrogen atmosphere based on thermo-gravimetric analysis (TGA) with multiple kinetic models. And clearly pointed out that its pyrolysis is divided into two stages: 276 -372°C for the removal of acetate groups, and 372-495°C for the polymer backbone breakage, and the complete kinetic parameters were given for the first time. Wang Min et al [7] further showed by thermogravimetric analysis (TGA) that EVA can achieve nearly complete decomposition with a weight loss of 99.6% when the temperature is increased above 515 °C in a nitrogen environment, and combined with kinetic parameter analysis revealed the energetic properties of the pyrolysis reaction in a nitrogen atmosphere. Tao et al [8] combined experiments with density flooding theory (DFT) calculations, and from the microscopic reaction mechanism, it was pointed out that EVA pyrolysis mainly generates gas-phase products such as CO₂, low molecular olefins and alkanes, which is of great significance for understanding the product distribution and optimizing the process parameters. Overall, the nitrogen pyrolysis process has the advantages of complete decomposition and high recovery purity, but it also has the problems of longer reaction time and higher energy consumption.

3.1.2. Air pyrolysis

Compared with nitrogen pyrolysis, combustion in air or oxygen-enriched environments improves the treatment efficiency by accelerating the EVA decomposition process, which is suitable for large-scale and rapid recycling needs. Huang et al [9] investigated the decomposition characteristics of EVA and TPT backsheets in an air atmosphere through thermogravimetric analysis, and pointed out that the complete removal of EVA could be achieved by treating the material for 30 min at 450 °C under a 20% O₂ atmosphere. And the Farrell et al. [10] further found that the pyrolysis of EVA in air atmosphere firstly releases acetic acid at ~360 °C, and then the main chain cracking occurs at ~470 °C. The products are rich in hydrogen, methane and carbon dioxide, and EVA has a high calorific value of 39.5 MJ/kg, which shows good potential for alternative fuels. EVA has a high calorific

value of up to 39.5 MJ/kg, showing good potential as an alternative fuel. In addition, Królikowski et al [11] proposed a process combining solvent cleaning and subsequent combustion treatment, which effectively reduces residual contamination and further improves the purity of the recovered material. Although the air combustion method has obvious advantages in terms of processing speed and simplicity, attention should be paid to controlling the potential damage of high-temperature oxidation on high-value materials such as silicon wafers.

3.2. Pyrolytic behavior of backsheet materials

Photovoltaic module backsheets are usually composed of multilayer polymer materials such as PET, PVDF, PVF, etc. Their pyrolysis behavior is of great significance for the design of the recycling process and environmental impact. According to the different atmosphere conditions, pyrolysis methods for backsheets can be mainly categorized into nitrogen pyrolysis and air combustion.

3.2.1. Nitrogen pyrolysis

The pyrolysis process of backsheet materials under inert atmosphere can effectively avoid oxidative reactions, which is suitable for the protective recycling of high-value materials. Wang Ruixue et al [12] investigated the pyrolysis behavior of TPT backsheets in waste crystalline silicon PV modules through a two-stage heating process. It was shown that the complete stripping of TPT backsheets could be realized by heating at 150°C for 5 min; subsequently, EVA adhesive film could be completely removed by pyrolysis in a nitrogen environment at 500°C, and the products were mainly low molecular hydrocarbons. In addition, Danz et al [13] studied the pyrolysis process of fluorine-containing backsheet materials (e.g., TPT and KPK) under nitrogen atmosphere, and found that TPT began to release fluorine at 300 °C. The release of fluorine reached the maximum at 500 °C, which indicates that fluorine is mainly released in gaseous form during the pyrolysis process, and it needs to be controlled in the actual operation.

3.2.2. Air pyrolysis

Under oxidizing atmosphere, the combustion process of the backsheet material is more rapid, but it may lead to the release of harmful gases. Danz [13] et al. further investigated the combustion behavior of TPT and KPK backsheets under air atmosphere, and found that these two materials almost completely released their fluorine content in the temperature range of 750-950°C. Mainly in the form of harmful gases such as HF exist, and an efficient exhaust gas treatment system is required to reduce environmental pollution. In addition, Farrell et al [10] evaluated the energy recovery potential of polymer materials in waste PV modules and found that the backsheet material has a high calorific value and can be used as an alternative fuel, but the harmful substances that may be produced during its combustion need to be considered.

3.3. Co-pyrolysis behavior of EVA and TPV

Chen et al [14] carried out a systematic study on the co-pyrolysis behavior of retired photovoltaic module encapsulation material EVA (EPV) and backsheet material TPV. As shown in Figure 1, Through the TG-DTG test at a heating rate of 20 °C/min, they found that the mixed molar ratio EPV:TPV =1 (hereafter referred to as ET1) samples showed obvious bimodal mass loss characteristics in the main pyrolysis region, which was significantly different from the single-peak curve of the single component. Indicating that there was a synergistic effect of the coexistence of

weakly facilitated reaction and inhibition of the two materials in the decomposition process. Further, the deviation of the actual mass loss of ET1 from the theoretically weighted value ranged from -1.51% to 3.07%; the synergistic effect of the two materials enhanced the decomposition rate in the interval of 452-472 °C, while they inhibited the decomposition process to some extent in the interval of 491-507 °C.

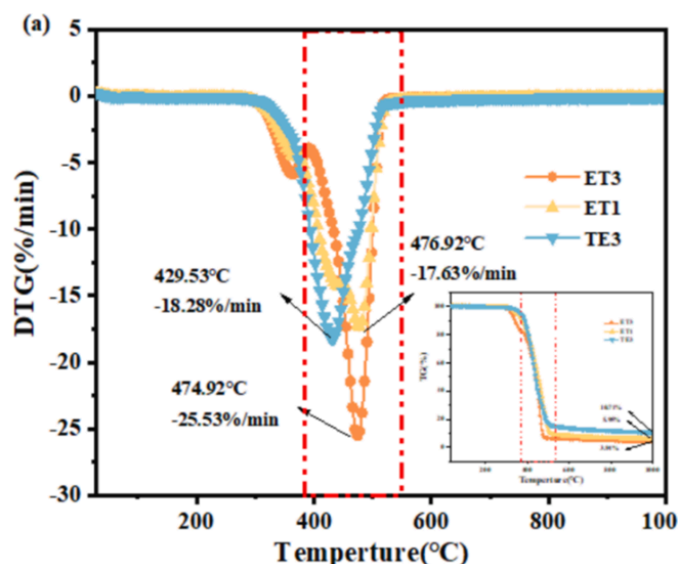


Figure 1: Heat loss curves of EPV and TPV mixtures with different ratios

As shown in Figure 2. Zhang et al. [15] deeply analyzed the interaction mechanism of EVA/TPT co-pyrolysis and the migration behavior of fluorine elements based on the TG-FTIR-MS coupling technique. The TG-DTG curves showed that the weight loss peak temperatures of the co-pyrolyzed samples generally shifted upward compared with those of the single components. The TG-DTG curves showed that the weight loss peak temperatures of the co-pyrolyzed samples were generally shifted upward by about 5-15 °C compared with those of the single component, and a significant negative synergistic effect was manifested in the range of 300-440 °C, whereas a positive synergistic effect appeared in the range of 440-500 °C, which implied that the H^+ produced by the EVA in the process of deacetylation could help to accelerate the de-fluorination reaction of TPT. In the FTIR spectra, the characteristic absorption peaks of HF in the region of 3600-3900 cm^{-1} were observed throughout the pyrolysis process, indicating the continuous release of HF. Co-pyrolysis lowered the initial release temperature of HF by about 90 °C, and elevated the total amount of the released amount by 32.3%. Meanwhile, the relative proportion of aromatic fluorination products was reduced from 100% to 58.8%. The results showed that the co-pyrolysis could significantly inhibit the generation of aromatic fluorinated compounds.

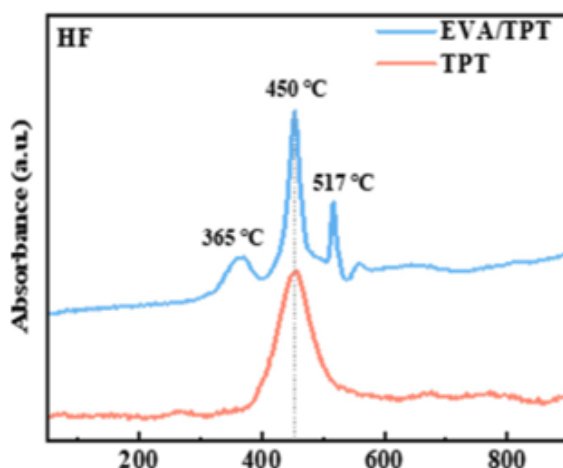


Figure 2: TG FTIR mapping of the temperature-dependent evolution of HF in fluorine-containing products during individual pyrolysis and co-pyrolysis processes

4. Conclusion and outlook

This paper systematically reviews the pyrolysis behavior of EVA adhesive film and backsheet materials in crystalline silicon photovoltaic modules under different heat treatment atmospheres. It is shown that pyrolysis under nitrogen can effectively avoid the oxidation of high-value metals, which is suitable for the protective recycling of materials; while the air combustion method has the advantages of easy operation and high efficiency, which is more suitable for large-scale processing needs. In addition, co-pyrolysis technology significantly improves pyrolysis efficiency and product quality through synergistic reactions between materials, especially in promoting the release of fluorine elements and inhibiting the generation of aromatic fluorine compounds. However, the release of harmful gases during high temperature treatment and the control of energy consumption are still technical challenges that need to be broken through in the future. In order to achieve green and efficient PV module recycling, it is suggested that subsequent research should strengthen the exploration of synergistic pyrolysis mechanism, product control and tail gas management, and promote the optimization of the coupling of experimental and process design.

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