The application of organic solvents and thermal process for eliminating EVA resin layer from waste photovoltaic modules

Wei Sheng Chen¹, Yen Jung Chen¹, and Yu An Chen¹

¹National Cheng-Kung University, Resource Engineering

qaz5932201@gmail.com

Abstract. With rapidly increasing production and installation, recycling of PV modules has become the main issue. In this study, we developed the application to recover the tempered glass from panels and remove Ethylene-vinyl acetate (EVA) from PV cells. The processes divided into two parts, organic solvents soaking and thermal treatment. In the organic solvents process, this study soaked PV modules into organic solvents to dissolve EVA resin and recover tempered glass. In the thermal treatment, this study removed EVA resin remaining on the PV cell. This study can comprehensively recover tempered glass and remove 99.97% EVA resin from PV cell. Moreover, it can contribute to not only subsequent leaching processes but also the environment and humankind health.

1. Introduction
The PV technology is considered to be one of the greenest and most promoting green energy-generating technologies as it generates electricity directly from the solar energy and therefore avoid fossil energy consumption and global warming gases emissions during energy production process. Over this decade, PV technology has shown the attempt to become the majority of green power generation for the world. According to 2018’s report, in 2017, 94.6GW PV modules were installed worldwide which represents 55% of newly installed renewable energy capacity. The Cumulative installation of PV panels achieved to 402GW in 2017. [1] However, the dilemma of PV system end-of-life (EoL) is now a big problem because of the lack of relevant PV modules recycling research. PV module average life, 20-25 years, reflects a large number of PV modules waste after 2030. According to the statistics, the mass of waste will reach 8.6k tons in 2049. [2] Additionally, the PV module contains hazardous materials such as Lead, Cadmium, Tellurium, Selenium, Silver which have caused serious health problems. [3] Therefore, the end-of-life PV modules should be recycled for the environment.

PV modules are mainly divided, Polycrystalline Silicon Solar PV (c-Si) and Thin-Film Solar PV (CdTe, CIGS, a-Si). Polycrystalline Silicon Solar PV (c-Si) account for 93% in PV modules, and the others account for 7%. The main issue of recovering PV modules is to eliminate the EVA resin layer which is used to become the adhesive layer on PV modules. This study mainly provides the process for the separation of the tempered glass and PV cells to recycle c-Si PV. Several solvents such as sulfuric acid, nitric acid, organic solvents (Alkane, Alcohol) were employed to separate tempered glass in other researches. [4][5] According to the literature review, the EVA resin can be easily removed by heating. [6][7]
In this study, the tempered glass was recovered by two alternative types of solvent, one for swelled EVA resin and one for dissolved EVA resin. The residual EVA was also removed by the thermal process.

2. Materials and experiment

2.1. Materials
PV modules are composed of aluminum frame (6.98%), tempered glass (74.1%), Ethylene-vinyl acetate (11.3%), Crystalline silicon batteries (6.81%), and Junction Box (1.3%). Fig.1 shows the schematic representation of the layers of the waste c-Si PV module of 1636x983mm2/18.5kg/250W which was used in this essay.

![Schematic representation of the layers of a crystalline silicon photovoltaic panel](image)

**Figure 1** Schematic representation of the layers of a crystalline silicon photovoltaic panel.

2.2. Organic solvent processes for c-Si recycling
The tempered glass and PV cells were separated organic solvents. There were three status performed, non-separated, swelled, and separated. After then, this study compared effective organic solvents for investigating the separation efficiency. This study screened two ways to recover tempered glass: separate directly organic solvents and swelled but need hand sorting organic solvents.

2.3. Thermal process
This study provided the thermogravimetric analysis graphs of pure EVA resin and PV modules. This process compared the main mass loss of PV modules and EVA resin to set the condition temperature for removing EVA resin from the PV cell. After the aforementioned process, the shattered PV cell with high purity of Silicon and valuable metal can make subsequent wet extraction techniques more efficient.

3. Result and discussion

3.1. Separation of the tempered glass and the PV cell using organic solvents
According to the experiment, the PV modules at the swelled status and separated status can easily remove the tempered glass from the PV cell. As the result, according to Table 1, Tetrahydrofuran, Toluene, Chloroform, and D-Limonene had a well-sorting effect on the separation between the
tempered glass and PV cell, while Acetone and Ethyl alcohol had no change. After the organic solvents process, the tempered glass can be easily removed and recycled. The recovery of tempered glass can reach 100%. According to Table 1 and Fig 2, D-Limonene and Toluene have the higher solubility of EVA resin. They spent less time completing the process of expansion and decomposition. Tetrahydrofuran and Chloroform cannot comprehensively dissolve EVA resin but can effectively swell it. In this case, this study screened two ways to recover tempered glass: separate directly organic solvents (D-Limonene, Toluene) and swelled but need hand sorting organic solvents (Tetrahydrofuran, Chloroform). Solvents can be selected for different requirements.

Table 1. Status of PV modules immersed by the organic solvents in 90°C

| solvent          | 1 min | 30 min | 1hr | 2hr | 24hr | 48hr |
|------------------|-------|--------|-----|-----|------|------|
| D-Limonene       | Δ     | ○      | ○   | ○   | ○    | ○    |
| Tetrahydrofuran  | X     | Δ      | ○   | ○   | ○    | ○    |
| Toluene          | ○     | ○      | ○   | ○   | ○    | ○    |
| Chloroform       | X     | Δ      | Δ   | Δ   | Δ    | Δ    |
| Acetone          | X     | X      | X   | X   | X    | X    |
| Ethyl alcohol    | X     | X      | X   | X   | X    | X    |
| X: non-separated | Δ: swelled | ○: separated |

Table 2. 6M, 40°C organic solvents for EVA solubility. Stir an hour.

| Solvent         | Weight change |
|-----------------|---------------|
| D-Limonene      | 21.14%        |
| Tetrahydrofuran | 13%           |
| Toluene         | 30.60%        |
| Chloroform      | 18.2%         |

Figure 2. Solubility increases with temperature.

3.2 Removal of the EVA resin by heat treatment
As Fig. 3 shown, after the separation process, EVA resin still remained on the PV cell. Heat treatment process was employed to remove EVA resin from the PV cell. Fig. 4(a) and (b) showed that EVA resin and PV modules both have a huge mass decline at 380°C [8]. When the temperature reaches 500°C, the weight of EVA resin approached zero. Therefore, it can be known that the EVA resin on the surface of the solar cell can effectively reduce the weight of the EVA resin after heating to 500°C.
The temperature of thermal treatment dropped to 500°C for 2 hours because of the power generation efficiency of Polycrystalline Silicon decline when the temperature heat over 500°C. [9] The temperature was raised to 900°C for 4 hours to eliminate all organic matter. After heating to 900°C for 4 hours [10], the weight change of the PV cell accounted for 0.028%. The consequent showed that this study removed 99.97% of EVA resin.

3.3. Characterization of the PV cell after recovering

The PV cell in our experiment mainly contains pure silicon, Aluminum Oxide, and Copper Oxide. Fig. 5 showed the peak of the PV cell, Si accounted for the most part of the PV cell. Table 3 showed the concentration of the PV cell. In cell recycling, interconnected cells are first immersed in a leaching solution to dissolve four metals, Al, Ag, Pb, and Cu. These metals are then recovered from the leaching solution one by one through electrowinning [11].

![Figure 3(a)](image1)
![Figure 3(b)](image2)
![Figure 3(c)](image3)

**Figure 3(a)** the PV cell surface after the swelling of EVA resin in microscopic view. **3(b)** EVA bubble resin remained on the PV cell. **3(c)** PV cell after thermal treatment. Nearly no bubble resin remained on the PV cell.

![Figure 4(a)](image4)
![Figure 4(b)](image5)

**Figure 4(a)**. EVA resin TGA analysis chart **(b)**. Waste solar panel TGA analysis

| metal | percentage |
|-------|------------|
| Si    | 36.19%     |
| Al    | 0.15%      |
| Cu    | 0.8%       |
| Ag    | 0.01%      |
| Pb    | 0.06%      |

**Table 3** Weight percentage of valuable metal in the PV cell
4. Conclusion
Organic solvents and heat treatment can effectively recover PV modules. This study gave two types of organic solvents for recovering tempered glass, separated and swelled. As a result, D-Limonene and Toluene made more effect on dissolved EVA resin and comprehensively recovered the tempered glass. This study set 500°C 2 hours for effectively eliminating EVA resin. The thermal process removed 99.97% EVA resin. This study can provide effective processes to treat the waste of solar panels containing tempered glass or EVA resin.

5. References
[1] T. Doi, I. Tsuda, H.Unagida, A.Murata, K.Sakuta, and K.Kurokawa, “Experimental study on PV module recycling with organic solvent method,” Sol. Energy Mater. Sol. Cells, vol. 67, no. 1–4, pp. 397–403, 2001.
[2] S.Weekend, A.Wade, and G.Heath, End-of-life management: Solar photovoltaic panels. 2016.
[3] M.Marwede and A.Reller, “Future recycling flows of tellurium from cadmium telluride photovoltaic waste,” Resour. Conserv. Recycl., vol. 69, pp. 35–49, 2012.
[4] V.Savvilotidou, A.Antoniou, and E.Gidarokos, “Toxicity assessment and feasible recycling process for amorphous silicon and CIS waste photovoltaic panels,” Waste Manag., vol. 59, no. August, pp. 394–402, 2017.
[5] S.Kang, S.Yoo, J.Lee, B.Boo, and H.Ryu, “Experimental investigations for recycling of silicon and glass from waste photovoltaic modules,” Renew. Energy, vol. 47, pp. 152–159, 2012.
[6] T.Doi, I.Tsuda, H.Unagida, A.Murata, K.Sakuta, and K.Kurokawa, “Experimental study on PV module recycling with organic solvent method,” Sol. Energy Mater. Sol. Cells, vol. 67, no. 1–4, pp. 397–403, 2001.
[7] A.Doni and F.Dughiero, “Electrothermal heating process applied to c-Si PV recycling,” Conf. Rec. IEEE Photovolt. Spec. Conf., pp. 757–762, 2012.
[8] A.Badiee, I. A.Ashcroft, and R. D.Wildman, “The thermo-mechanical degradation of ethylene vinyl acetate used as a solar panel adhesive and encapsulant,” Int. J. Adhes. Adhes., vol. 68, pp. 212–218, 2016.
[9] E.Technology, Y.Yuan, C.Materials, and Z. N.Road, “Silicon Resource Recovery of Spent Monocrystalline Silicon Solar Batteries,” pp. 9–13, 2012.
[10] A. Marcilla, A. Gómez, and S. Menargues, “TG/FTIR study of the thermal pyrolysis of EVA copolymers,” J. Anal. Appl. Pyrolysis, vol. 74, no. 1–2, pp. 224–230, 2005.
[11] W. Huang, W. Jung, L. Wang, W. Sun, and M. Tao, “Strategy and technology to recycle wafer-silicon solar modules,” Sol. Energy, vol. 144, pp. 22–31, 2017.

Acknowledgments
This study was supported by National Cheng-Kung University Dept. of Resource Engineering, R.O.C.