Industrial Engineering Journal
ISSN: 0970-2555
Volume : 53, Issue 4, No. 1, April : 2024

THERMAL DELAMINATION OF END-OF-LIFE (EOL) PHOTOVOLTAIC SOLAR (PV) MODULE TO FACILITATE RECYCLING

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Abstract: Solar Photovoltaic (PV) module technology is the most prominent, well-established, and mature source of producing renewable energy. A detailed analysis of the gases evolved during pyrolysis of the End-of-Life (EOL) crystalline silicon photovoltaic (c-Si PV) solar module, focusing on recycling strategies has been reported herein. PV modules encapsulated with Ethylene-vinyl acetate (EVA) – with and without Poly-vinylidene fluoride (PVDF) polymer backsheet were pyrolyzed at 500°C and evolve gases was collected in the gas cell.
The current installed capacity in India is approximately 67 GW. As per a report by a European agency, in April 2022, globally cumulative installed PV capacity has crossed 1TW. PV module installations in india are expected to rise further to 20 TW by 2050. But over the next decade, the problem will magnify exponentially. Such end-of-life (EOL) PV installations are treated as solar waste and they need to undergo a carefully strategized waste recycling route in order to keep the overall carbon and pollution footprints to a bare minimum and to propel the circular economy in the PV sector.

1.1 Introduction & Problem statements

Harnessing solar energy through the PV module (Photovoltaic effect) to produce electricity has now become the fastest-growing sector in the renewable energy production industry [1]. A Typical PV module consists of Si solar cells connected in rows and columns by solder and interconnects rails (fig. 1). The solar cells are encased in an encapsulant (typically Ethylene Vinyl Acetate, EVA) and fused to glass on the front and with a backsheet. The entire structure is encased in an Aluminum frame. There is a junction box on the backside for making the electrical connections. Photovoltaic modules work for almost 25-30 years before they are no longer usable due to reduced efficiencies. India's annual PV additions achieved a record in 2022 at 18 GW, up 27% from 2021 (Fig. 2). Modules installed in the early 2000s are already reaching end-of-life, and the numbers will rapidly increase soon. In India, the PV module waste is expected to reach 200,000 tonnes by 2030 and 1.8 million tonnes by 2050 annually [Figure 3]. IEA reported that in 2022, 231 GW of PV was installed globally, bringing cumulative PV installs to 1.2 TW. The worldwide estimated Solar energy target by 2030 is 16 TW (fig. 4) and same tonneage estimated Solar Waste will be 78 million tons (fig. 5). As the installation of PV modules increases exponentially, the End-Of-Life modules are also expected to rise by the same proportion shortly. Despite the obvious environmental benefits, it is difficult for PV module recycling to be widely accepted due to economic constraints, namely, the low value of recovered material and high recycling cost [2-4]. The lack of PV-specific disposal guidelines, technical know-how, and low industrial involvement further add to this burden. Thus, decommissioned panels are primarily being dumped in landfills or, at best, being sent to glass recyclers.

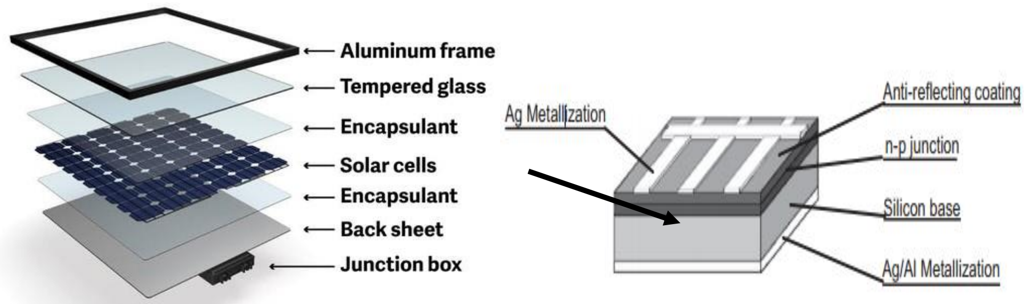

Figure 1. Solar module basic structure, and types of material used in solar cell [1].

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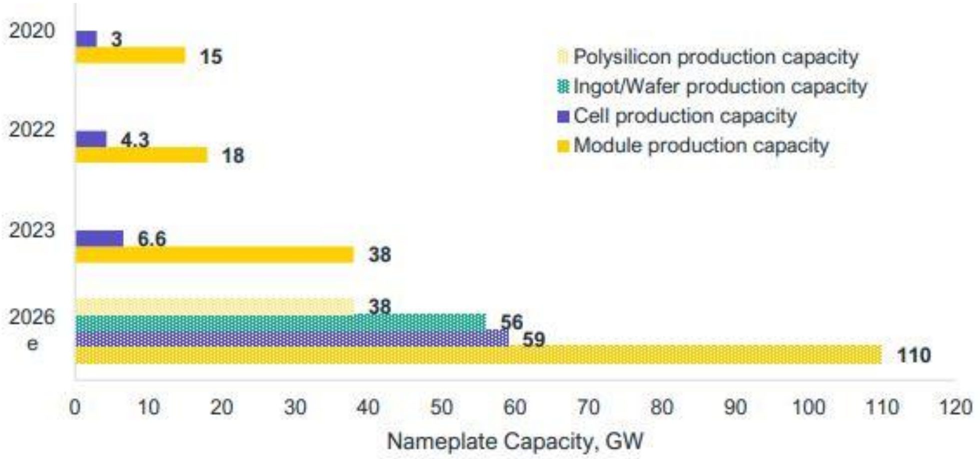

Figure 2. Growth of Domestic PV Manufacturing Capacity in India [2]

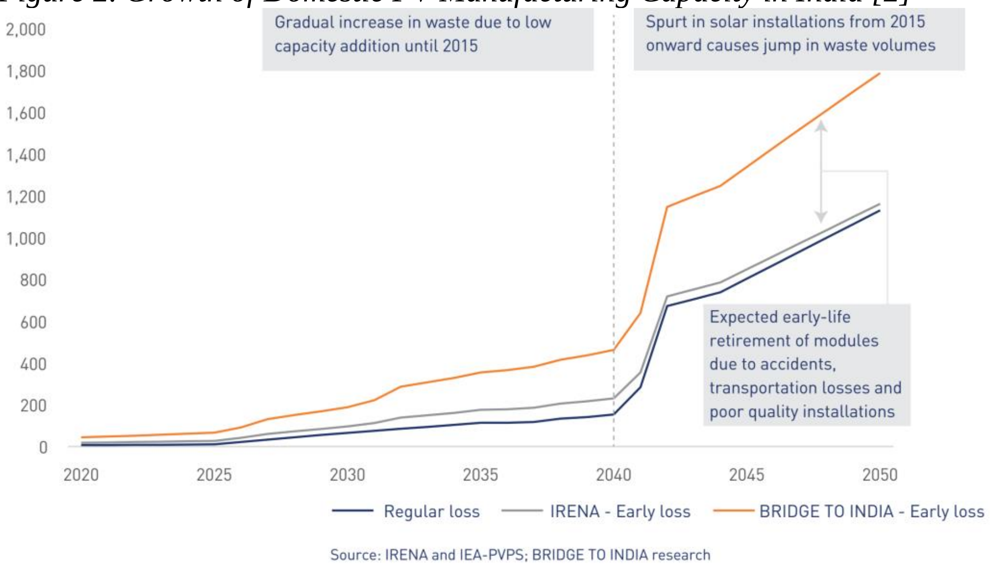

Figure 3: Estimated annual PV module waste generation in India (In thousand tonnes)[3]

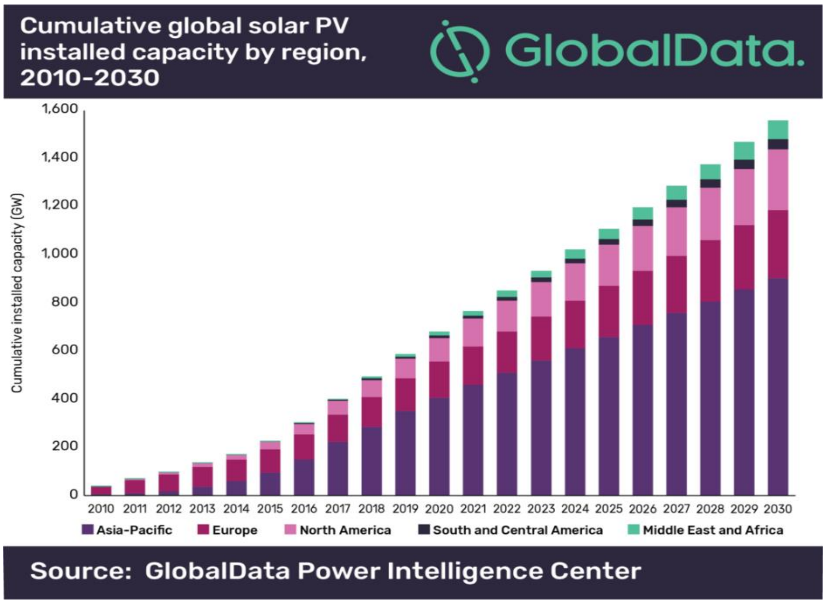

Figure 4: Globally cumulative installed c-Si PV module [2]

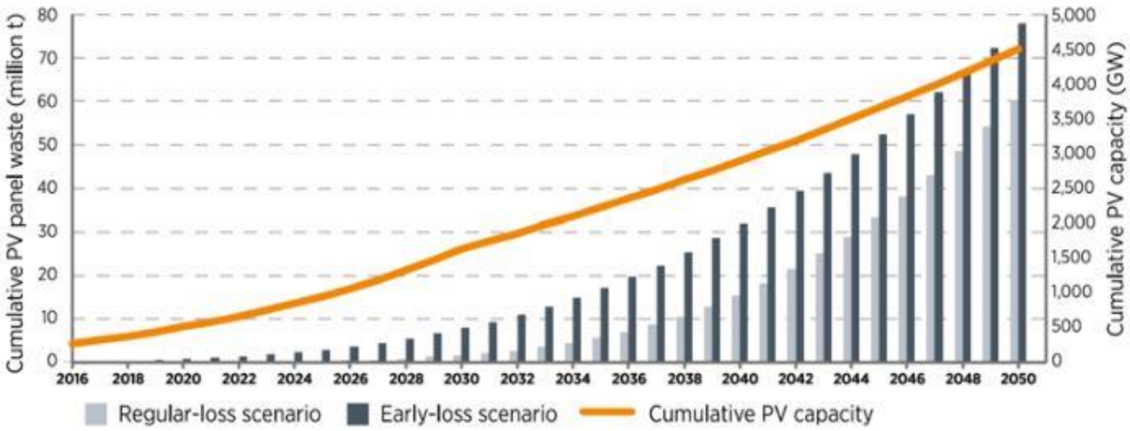

Figure 5: Globally cumulative c-Si PV module waste [3-4]

The Si modules' weight is primarily due to the Glass (Tempered, textured, low Fe) and the Al frame. The Si constitutes about 3% of the total weight, and the Ag is in minuscule quantity [Table 1]. The revenue figure noted here and in the sections below do not include any of the associated costs incurred in the process.

Table 1: Potential revenue by material extraction from a 60-cell 250 W Al BSF module of dimensions 1m x 1.7m, weighing approximately 17 Kg. As of 30 October 2019, $10.61/module [Adapted from [4-5]]

Material	Weight %	Weight	% Recovery	Price ($/kg)	Value ($/module)	% Total
Glass	78.36	13.5 kg	100	0.1	1.35	12.7
Al	10.62	1.83 kg	100	0.95	1.74	16.4
Polymers	6.85	1.18 kg	0		0	0
Si	3.25	0.56 kg	90	5.52	3.09	29.1
Ag	0.04	6.5 g	100	574.23	3.73	35.2
Cu	0.63	0.11 kg	100	5	0.55	5.2
Pb	0.1	18.3 g	100	1.1	0.02	0.2
Sn	0.13	21.9 g	100	6.06	0.13	1.2
Total					10.61	100

1.2 Recycling techniques

The recycling methods are essentially a combination of Mechanical, Thermal, and Chemical methods [1-5]. The processes chosen depend on the requirement of the end products.

The Aluminum frames are removed by mechanical means by physically separating from modules. The encapsulants are usually unrecoverable. They are usually pyrolyzed by heating to approximately 500°C. The other option is to dissolve it chemically in organic solvents. The key challenge here is either the generation of gaseous exhaust from polymer pyrolysis or the disposal challenge of large quantities of organic solvents [6].

Thermal Delamination: EVA has a burnout temperature of Approximately 450°C. The conventional Fluoro polymer-based back sheets burn out at ~ 550 [Figure 9]. The reported thermal decomposition involves heating the modules to 200°C. At this temperature, the Back sheet is still intact but can be peeled off. The remaining structure of Si Cell encased in EVA stuck to glass is heated to 480°C at a ramp rate of 15°C /min for 30 minutes to burn off the EVA [4, 7].

Chemical treatment for delamination: There are some reports of chemical approaches being employed for the delamination of PV modules. It has been reported that Toluene or HNO_3 gives the best results, but the process takes up to 2 days at 90°C [3, 6]. The disposal of the effluents also needs

to be done appropriately. Clearly, this method is not sustainable. Hence it is not being discussed in detail here.
Other delamination methods: Such panels have been delaminated using a wire saw, or even a knife after softening the encapsulant by heating the module on a hot plate at 120°C [5-6]. Another method reported uses a knife heated to 300°C to locally soften the EVA and peel it off from the glass (Figure 6). This method is being used by industry in Japan [5].

Figure 6: Removal of the back sheet from a Thermoplastic encapsulant based module [5].
Glass removal: The glass used in PV modules is low Fe, Tempered, and Textured Glass. It is the primary recoverable material in a module. Most recycling operations simply crush the module into small pieces of glass with Si and encapsulant stuck to them.
Solder is usually removed thermally or chemically. Though Lead-free solders have been developed, the PV modules still use lead-containing solder, especially the modules which are expected to come for recycling over the next few decades. Depending on the local legislative requirements, these may need to be recovered. Interconnects are usually easily recovered once the solder is removed. These can be easily collected and recycled as Al or Cu [5-9].
It is a well-known fact that recycling is generally not a highly profitable activity (as reported *Table 1*). However, it is imperative that recycling is done nonetheless to minimize the environmental impact. With this in mind, project aims to develop low-cost, less complex methods which have recovery products with good commercial value. We are glad to report that our preliminary cost-benefit analysis indicates that our recycling process is significantly profitable, without even accounting for the environmental benefits or resources saved by not dumping in landfills and carbon credits.

3.1 Detailed Outcomes:
- Demonstration of module delamination by various methods – Chemical/Thermal/Physical
- Recovery of module components – Glass, Solar cell (Intact or broken)
- Reuse – If the intact glass is recovered, attempt re-manufacture of a fresh panel
- Recovery of Al, Ag from the Solar cell by chemical leaching:

– Leaching Al exclusively, from the PV cells in to the leachate
– Recovering metallic Al/ Al compound
– Leaching Ag exclusively, from the PV cells in to the leachate
– Recovering commercially pure Ag/ Ag compound
– Recovering silicon, PV cell base material as bare as possible

4.1 Result & discussions:
One of the key challenges in PV module recycling is delamination, i.e., the removal of the solar cell, solar glass, and backsheet. I have successfully delaminated mini modules and separated the solar glass, solar cells, and backsheet by thermal pyrolysis [findings has been reported and accepted, 8]. Figure 8 shows the flow chart of previous work carried out and some findings are reported herein. The recovered

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Solar glass can either be used to manufacture new modules – possibly for household and distributed power generation or channeled into the glass recycling process.

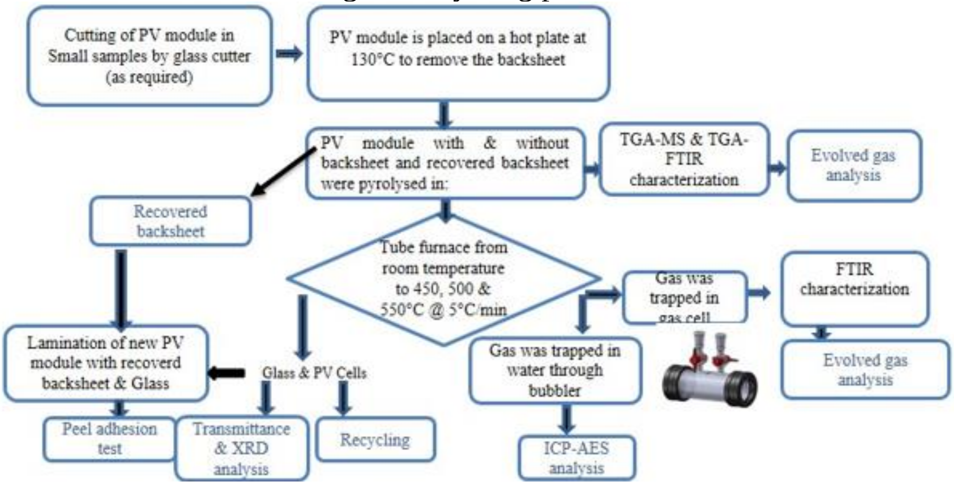

Figure 8. Flow chart of previous work carried out and proof-of-concept

Figure 9 illustrates FTIR spectra of gases collected during pyrolysis of PV module without backsheet at 450°C, 500°C, and 550°C. The FTIR peaks of various functional groups could be observed; viz. CO_2, HCN, acetic acid and CO at their respective wavenumbers. The emitted gas at 450°C showed a less intense peak of CO_2 which can be considered almost nil as compared with other evolved gases; however, the higher emission of CO and HCN must be noted here. Further, with an increase in the pyrolysis temperature to 500°C, and 550°C, the emission of fumes and gases is seen to be increased along with the increased formation of CO_2. From an environmental point of view, CO is considered more hazardous than CO_2. Hence, the authors suggest that pyrolysing PV module, after removal of backsheet, at 500°C is more environmentally friendly than subjecting the same to 450°C or 550°C either. Figure 10 Demonstrate that valuable materials, Namely Ag, Al, and Si, can indeed be removed from discarded solar cells.

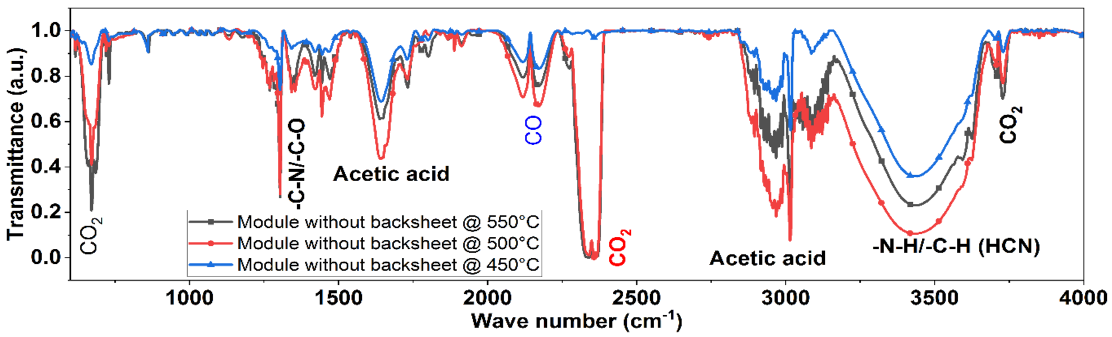

Figure 9. FTIR spectra of fume collected during pyrolysis of PV module without backsheet at 450°C, 500°C and 550°C [8]

Conclusion: The summary of previous experimental works are as follows:

1. At 130°C the PVDF backsheet was manually removed from the PV module.
2. EVA encapsulation has a two-steps degradation whereas PVDF backsheet has one-step degradation.
3. At 500°C, there is minimal reduction in the transmittance of the solar glass as it retains 90% Transmittance.
4. The major pyrolyzed evolved gases were appeared at temperatures ranging from 350-470°C.
5. The emission of gases during pyrolysis of PV module are much higher in volume as well as in entities as compared with PV module without backsheet.

6. Compositional analysis of pyrolyzed gas after passing through bubbler.
7. Furthermore, the emission of gases are less when pyrolysis at 500°C rather than 450°C and 550°C.
8. The emission of toxic gases such as; Fluorine, C_2H_6, CH_4, and HF were exclusively observed during pyrolysis of the PVDF backsheet.
9. The peel adhesion strength of recovered backsheet & glass laminated with EVA is less as compared with new backsheet & glass laminated with EVA .
10. Determination of the most suitable thermo-mechanical-chemical process and leaching chemistry for the maximum dissolution of the metal under consideration. The chemistry and processing conditions for the metals, Ag, Al, and Si are identified.

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