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Encapsulant Materials and Their Adoption in Photovoltaic Modules: A Brief Review

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Abstract: In the last two decades, the continuous ever growing demand for energy has determined a significant development in the production of photovoltaic (PV) modules. Anyway, a critical and very important issue in the module design process is the adoption of suitable encapsulant materials and technologies for cell embedding. Therefore, adopted encapsulants have a significant impact on modules efficiency, stability and reliability, and to ensure the unchanged performance of PV modules in time, the encapsulant materials must be selected properly. The selection of encapsulant materials must maintain a good balance between the encapsulant performance in time and costs, related to materials production and technologies for cells embedding. However, the encapsulants must ensure excellent isolation of active photovoltaic elements by the environment, preserving accurately the PV cells against humidity, oxygen and accidental causes that may compromise the PV modules function. This review provides an overview of different encapsulant materials, their main advantages and disadvantages in adoption for PV production, and also in relation to used encapsulant technologies for cell embedding, additives and the interaction of these materials with other PV components.

Keywords: PV modules; encapsulant materials; cost-performance balance; cells preservation

1. Introduction

A new energy-consuming society requires more and more energy and its recovery by renewable sources becomes imperative. Therefore, the need to provide green energy is related not only to the growth request for energy but also to growing socio-political concerns and urgent action on a global scale to limit climate change. The requests to replace fossil-based resources and to reduce CO2 emissions could be obtained through the decarbonization of the energy sector. [1–3]

However, the worldwide capacity in green energy production has increased by up to 650 GW in the last 10 years, leveraging solar energy, being its cleanest and fastest-growing renewable energy sour. [4,5] The capture of solar heating, solar photovoltaic and solar thermal electricity required the development of advanced devices and technologies, but in all cases, the formulation of innovative and more efficient materials is absolutely required. [6–8]

In the last two decades, to convert efficiently the sun's energy into electrical energy, PV module design and production have been significantly advanced, and the growth trend in this field is mainly oriented to produce lighter and low-cost PV modules. The key factors for PV modules development and market penetration are their conversion efficiency, durability and stability. Therefore, the current operating life of a PV module is less than 25 years, while the latest generation of double-sided heterojunction photovoltaic panels, produced by 3SUN (ENEL Green Power, Rome, Italy), can maintain high properties and performance for about 35–40 years [9].

Crystalline silicon (c-Si) PV modules are mostly produced and commercially available photovoltaic devices and they consist mainly glass-encapsulant-cells-encapsulant-backsheet.

Extremely important components in PV modules are the encapsulant sheets based on polymer materials treated to obtain resistant structures that are able to prove mechanical stability, electrical safety and protection of the cells and other module components from environmental impacts. [10–17]

Although this review mainly addresses encapsulant polymeric materials that are used in making the PV module, it is also relevant to mention the manufacturing sequence for crystalline silicon wafers which constitutes the substrate of most solar cells today. The manufacturing sequence for crystalline silicon wafers can be divided into three steps that are (i) silicon feedstock, (ii) crystallization and (iii) wafering. However, the refinement processes for the hyper-pure silicon material were developed to enable the semiconductor industry. Although the silicon feedstock comes with purity more than sufficient for solar cells, the morphology of the micrometric-sized silicone crystals must be changed because of their extremely high brittleness. For this reason, the silicon material must be mandatory melted and re-crystallised under controlled conditions to generate larger crystal grains that are bonded and to minimize the crystal defects that could limit and compromise the solar cells performance. The transformation of silicon ingots to thin layers is carried out using slicing technologies, that are changed overtime, also in the presence of some colling media. [15]

Therefore, the crystalline silicon (c-Si) PV modules consist mainly glass – encapsulant – cells – encapsulant - backsheet, and currently, the backsheet is substituted by glass or plastic sheet to increase the solar capture efficiency, see Figure 1. Based on information available everywhere, as summarized in Figure 1, the evolution of Si-PV module technologies and devices develops toward lighter and low-cost efficient PV modules, as well as using innovative and high-performance materials. Therefore, thin-film PV modules are designed similarly to c-Si modules, and also for thin-film PV modules, the use of encapsulants is imperative to ensure efficient isolation of the PV components from exterior impacts. [18–34]

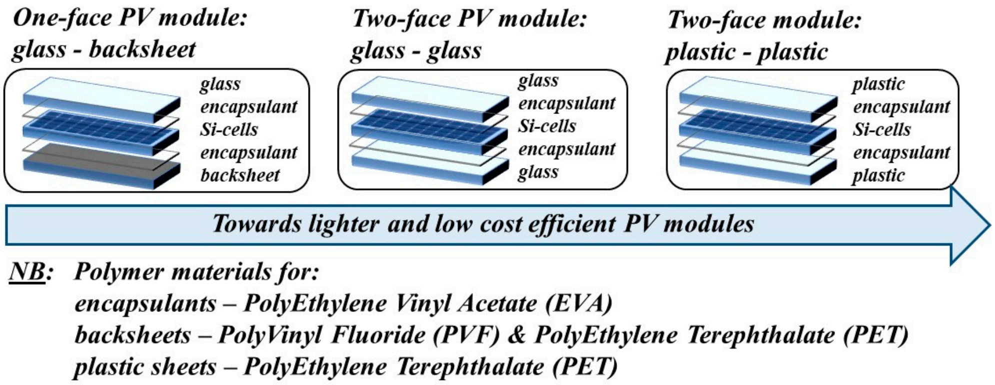
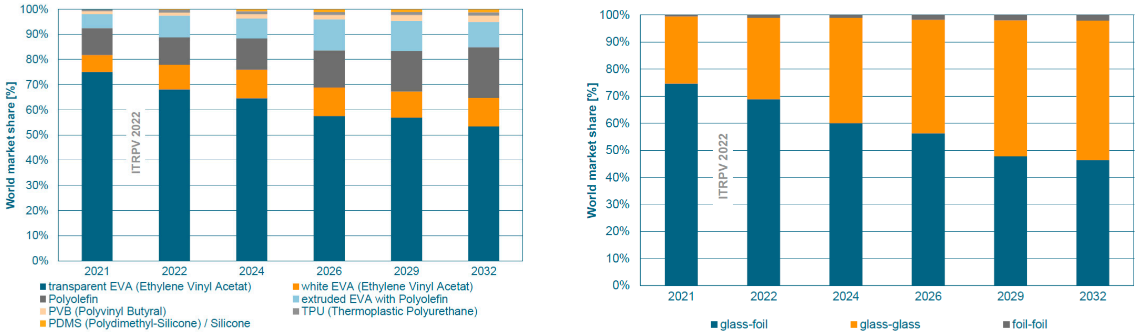


Figure 1. Evolution of Si-cell PV module technologies/devices.

However, as discussed accurately in International Technology Roadmap for Photovoltaic (ITRPV) – 2022 [35], the encapsulant and backsheet/cover are key component materials and both are also major cost contributions in PV manufacturing. Obviously, the balance between production costs and insurance of the module service lifetime must be mandatory established. Based on data available in the ITRPV report, EVA is the most considered and widely used encapsulant material, as shown in Figure 2a. [35] There is expected that EVA will keep a quite constant market share of about 10% over the next years. It is important to note that polyolefins are one incoming alternative to EVA, especially, if there are considered tow-face plastic-plastic modules and Si- heterojunction PV modules. Interestingly, as shown in Figure 2a [35], an increasing market share for polyolefins ca. is expected 20 times in the next 10 years, while for other encapsulant materials is estimated to keep a low market share for these specific niche applications.

It is worth noting that the foils will stay mainstream as back cover, although, for bifacial c-Si modules, it is expected that the glass will gain a significant market share as backsheet cover materials. There is estimated to have ca. 45% share in the next 10 years, see Figure 2b. [35]



(**a**) (**b**)

Figure 2. World market share for (a) different encapsulant materials and (b) glass and foil as front and back cover materials. Based on data from International Technology Roadmap for Photovoltaic (ITRPV) – Report 2022 [35].

However, over time, different polymer materials have been considered to produce PV modules, and currently, mostly popular encapsulants are based on (i) elastomers, such as poly-ethylene-vinyl-acetate (EVA) and silicones, (ii) thermoplastics, such as polyvinyl butyral (PVB) and ionomers, (iii) thermoplastic elastomers, such as thermoplastic silicone elastomers (TPSE), thermoplastic polyolefins (TPO), polyolefin elastomers (POE). Therefore, this review would provide an overview of the before mentioned different encapsulant materials, their main advantages and disadvantages in adoption for PV production, and also in relation to used encapsulant technologies, additives and the interaction of these materials with other PV components.

2. Encapsulant materials

The encapsulant polymer-based materials in PV-modules must provide proven mechanical stability, electrical safety and protection of the cells and other module components from environmental impacts. Therefore, mostly considered materials for encapsulants at the industrial scale are: (i) elastomers, such as poly-ethylene-vinyl-acetate (EVA) [18–20,27,28,32,36–38] and silicones [39–46], (ii) thermoplastics, such as polyvinyl butyral (PVB) [47–49] and ionomers [50–52], (iii) thermoplastic elastomers, such as thermoplastic silicone elastomers (TPSE) [53], thermoplastic polyolefins (TPO) [54,55] and polyolefin elastomers (POE) [37,38,56], because of their good balance between the performance and costs. Besides, to achieve even better performance in PV protection, all these polymer encapsulants must be processed by appropriate technologies to ensure accurate cells embedding and ribbons protection and must be added with suitable additives, such as crosslinkers, stabilizers and adhesion promoters. Therefore, the main technical specifications of encapsulant polymeric materials include melting and glass transition temperatures, volume resistivity, moisture transmission rate, light absorption, and elastic modulus.

Figure 3 shows a classification of the encapsulant polymeric materials, based on their chemical structures and bonds to form chemical or physical crosslinking structures of encapsulant films, while below all these encapsulant polymeric materials are shortly discussed and Table 1 summarizes the main physical properties of the PV-modules encapsulant materials and their advantages and disadvantages in adoption as encapsulant protection films.

Table 1. Mostly considered encapsulant materials for PV modules production, their main physical properties and main advantages and disadvantages.

Encapsulant materials	Main physical properties (*)	Advantages (+)	Disadvantages (-)
Elastomers			
EVA	Tg = -30/-40 °C E = 65 MPa RI = 1.48-1.50	(+) good balance performance/costs (+) easy cell encapsulation (+) random radical crosslinking (+) good compatibility with additives, such as UV adsorbers, stabilizers and antioxidants	(-) discoloration and yellowing (-) acetic acid formation as degradation product (-) EVA degradation products could react/interact with degradation products of stabilizers & antioxidants
Silicones	Tg = -40/-50 °C E = 10 MPa RI = 1.35-1.50	(+) excellent chemical inertia, oxidative and thernal resistance (+) very good transparency in UV range	(-) specific processing conditions and equipment (-) reinforcement additives must be used to improve the mechanical resistance (reduced mechanical resistance)
Thermoplastics			
PVB	Tg = +10/+20°C E = 10 MPa RI = 1.48	(+) current formulations based on PVB required bland vacuum lamination conditions (+) thermal stability and reduced aging rate (+) good transparency in UV range and low cost	(-) water uptake and hydrolysis (-) firstly, considered formulations required high pressure and temperature during roll-to-roll lamination, combined with autoclave (-) use of different additives
Ionomers	Tg = +40/+50°C E = 280 MPa RI = 1.49	(+) very good UV resistance (+) very good mechanical performance	(-) high production (synthesis) costs (-) specific processing conditions and equipment
Thermoplastic elastomers			
TPSE	Tg = -100 °C E = 250 MPa RI = 1.42	(+) excellent mechanical properties in the large temperature range (+) good electrical insulation (+) physical crosslinking through hydrogen bonds	(-) high synthesis and production costs (-) specific lamination conditions
TPO	Tg = -40/-60 °C E = 30 MPa RI = 1.48	(+) good mechanical performance and UV resistance (+) low synthesis and production costs	(-) high water permeability (-) chemically crosslinked TPO shows discolouration and reduced UV resistance
POE	Tg = -40/-70 °C E = 55 MPa RI = 1.48	(+) low synthesis costs (+) good elasticity and toughness	(-) reduced adhesion ability (-) chemically crosslinked POE shows discolouration

	(+) good UV resistance and no discolouration	

Note: (*) Tg – glass transition temperature; E – elastic modulus; RI – Refractive Index. The values are based on available literature.

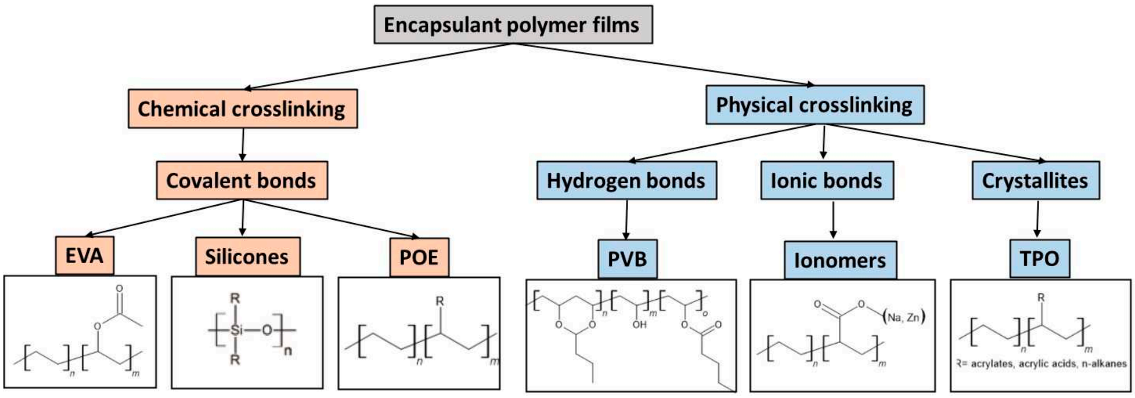


Figure 3. The encapsulant polymeric materials in PV-modules and their characteristics.

2.1. Elastomers as encapsulant materials

2.1.1. Poly-Ethylene-Vinyl-Acetate (EVA)

EVA is the most considered encapsulant material in the last twenty years, but although its formulation has been significantly improved, it shows drawbacks related to discolouration and yellowing. [18–20,26–28,32,36–38] As documented, EVA degradation phenomena have been extensively studied and described, and according to the literature, it degrades by deacetylation, hydrolysis and photothermal decomposition. [18–20,26] Besides, the photothermal degradation of EVA could be accelerated because of the photothermal degradation of additives such as UV absorbers, stabilizers and antioxidants.

However, the degradation of EVA and its additives is also accelerated by the formation of hot spots due to the presence of some Si-cells defects, which causes a local temperature increase, up to ca. 350 °C [57], and unfortunately, this causes an uncontrolled acceleration of EVA and additives thermal degradation/ decomposition and acetic acid formation. As documented in the literature, the thermal degradation of EVA, although in a reduced way, could be slightly slowed down by introducing polyolefin constituents. [26]

To be a good encapsulant, EVA must be transformed in elastomer by adding of suitable crosslinking agents and subjected to prolonged thermal treatment and high pressure. The peroxide radical crosslinking of EVA is a random process, and its occurrence must happen during the lamination process, considering the high volatility of low molecular weight crosslinkers.

Therefore, the EVA is considered a good encapsulant material also because of the good balance of performance and costs. Unfortunately, easy degradation of EVA, with the formation of acetic acid, discolouration ad yellowing, complies with the production of PV modules to search for other encapsulant materials having good balance performance/costs.

2.1.2. Silicones

There are inorganic-organic materials based on silicon, hydrogen and oxygen atoms (-Si(X,Y)-O-). [39–46] Although there are very promising materials, the high cost and request of highly specialized equipment for their lamination process, silicon materials are not considered for large-scale applications. These encapsulant materials are more suitable for special conditions applications, for example, for encapsulation of devices for extra-terrestrial use and applications. As widely known, the silicones show excellent chemical inertia and resistance to oxidation and heat, good transparency

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on UV range and very low water uptake. Unfortunately, due to the silicone nature, these encapsulant materials required specific processing conditions and equipment and for these reasons, their use could be justified considering high costs and high-performance applications. Besides, these materials show very low mechanical resistance and there is imperative the use suitable reinforcement additives, that could penalise the optical properties.

2.2. Thermoplastics as encapsulant materials

2.2.1. PolyVinyl Butyral (PVB)

The second most considered encapsulant material is PVB, having costs similar to that of EVA. [47–49] The firstly considered formulation of PVB for encapsulants required high pressure and temperatures during the roll-to-roll lamination combined with autoclave, and currently, upon accurate correction of PVB composition could be laminated considering bland conditions, lower temperatures and low time vacuum lamination, that makes PVB encapsulants mostly easy to process.

Therefore, the PVB show good thermo- and photo-oxidative resistance in comparison to EVA, although the use of different additives is absolutely requested to have low pressure and temperature processing. Additionally, PVB shows a high hydrolysis tendency due to its water uptake, and obviously, this represents a limit issue for its large-scale use.

2.2.2. Ionomers

There is a new high-cost class of PV modules encapsulants that are based on ethylene and unsaturated carboxylic acid co-monomers, such as ethylene-methacrylic acid copolymer. [50–52] Ionomers have high production costs for synthesis and in the last ten years, due to their good UV stability, have been considered suitable materials for different wire and cable applications. The ionomers form physical-crosslinked structures, due to their polar nature, and there is no requested chemical crosslinking. Based on the chemical nature of considered co-monomers, in some specific cases, could be required prolonged processing time in order to ensure good adhesion between the encapsulant sheets and cells. Ionomers show good mechanical performance and resistance and until now, they have been considered for thin-film solar modules, but there are promising encapsulants also for c-Si modules.

2.3. Thermoplastic elastomers as encapsulant materials

2.3.1. Thermoplastic Silicone Elastomers (TPSE)

These relatively new kinds of encapsulant materials combine good silicone performance and easy thermoplastic processability. [53] Until now, their synthesis and production costs are relatively high and for this reason, they are not considered for large-scale applications, but could be considered promising candidates for special PV-modules applications. The TPSE could form physical crosslinking structures and controlling the sequence and length of plastic and elastomer units could be obtained excellent mechanical performance, water permeability and electrical insulation. Besides, including more silicone units, there is possible to synthesize materials having a good resistance in large temperature ranges.

2.3.2. Thermoplastic Polyolefin (TPO)

As an alternative to EVA encapsulant, thermoplastic polyolefins (TPO) are newly developed non-crosslinking or crosslinking materials for photovoltaic (PV) module lamination. [54,55] According to the literature, the TPO show a lower discolouration tendency, and better optical and thermal properties degradation before and after artificial weathering. [55] Obviously, this makes these encapsulant materials very attractive, although some problems, related to good adhesion between the encapsulants sheets and cells during laminations, have been encountered. The TPO encapsulants are copolymers based on ethylene-propylene rubber and ethylene-octene rubbers and their synthesis and production are cheaper than other encapsulant materials. The TPO show also good mechanical properties and UV resistance and according to the literature, the discolouration of TPO is around nine times slower than that of EVA, and in 50 days of weatherability tests, the transmittance of EVA significantly reduced while TPO remained almost unchanged. Unfortunately, TPO shows water permeability significantly higher than EVA. Besides, some crosslinking TPO shows better adhesion properties, and similarly to EVA, they show discolouration and reduced ageing resistance. Fortunately, the degradation pathways do not develop volatile by-products, such as acetic acid, that could cause the corrosion of metal ribbons.

2.3.3. Polyolefins Elastomers (POE)

The POE are copolymers of ethylene and other alpha-olefin, such as butene or octene and there are very promising encapsulant materials. [37,38,55,56] The POE could be synthesized using metallocene catalysis, controlling the ethylene/comonomer sequence and comonomer content could be produced polymers with tailored elasticity. The presence of comonomer units disrupts the polyethylene crystallinity while the macroscopical mechanical behaviour of POE could be controlled by manipulating the molecular weights. Additionally, the POE show very good resistance to UV ageing and no discolouration upon sunlight, but unfortunately, there is required the use of adhesion promoters to improve the adhesion with glass and cells embedding.

Summarizing, the main physical properties of above discussed PV-modules encapsulant materials and their advantages and disadvantages in adoption as encapsulants are listed below in Table 1.

As mentioned before, in case of accidental “hot-spot” formations, due to incorrect PV-modules function, local temperatures arise up to ca. 350 °C and obviously, this issue is an enormous problem for all organic encapsulant materials. Especially for EVA this problem is extremely exacerbated because of favourable conditions for acetic acid formation and volatilization, causing sheets delamination and ribbons corrosion.

3. Technologies for PV-cells embedding

The solar cells can be embedded between encapsulant sheets using different technologies, specifically, vacuum lamination process, roll lamination, combined with autoclave, and casting process, as summarized in Table 2. [58–60]

Table 2. Currently adopted technology for PV-cells embedding.

Technology for cells embedding	Encapsulant materials	Processing conditions
Vacuum lamination	EVA, PVB, TPSE, TPO, POE ionomers	$T_{processing}$ = 140-170 °C $t_{processing}$ = 7-20 minutes
Roll-to-roll lamination, combined with autoclave	PVB, TPSE	$T_{processing}$ = 140-170 °C $t_{processing}$ = 7-20 minutes
Casting process	silicones	$T_{processing}$ = 80 °C $t_{processing}$ = 20 minutes

Therefore, the most considered processing technology is the vacuum lamination process that is adopted successfully for almost all encapsulant materials, such as poly-ethylene-vinyl-acetate (EVA), polyvinyl butyral (PVB), thermoplastic silicone elastomers (TPSE), thermoplastic polyolefins (TPO), polyolefin elastomers (POE) and ionomers. The processing conditions, such as temperatures and time for treatment, during vacuum lamination process, are chosen considering the chemical nature of encapsulants and they are usually $T_{processing}$ = 140-170 °C and $t_{processing}$ = 7-20 minutes.

The roll-to-roll lamination process, combined with autoclave, which is very similar to concept for glass lamination, is suitable for the processing of polyvinyl butyral (PVB) and thermoplastic

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silicone elastomers (TPSE) and there are considered processing conditions similar to that of the vacuum lamination process, i.e., $T_{processing}$ = 140-170 °C and $t_{processing}$ = 7-20 minutes.

The casting process is adopted for PV assembling when silicones are considered efficient encapsulant materials. It consists of a dispersion of silicones on components and then, the silicones form three-dimensional structures upon thermal or ultraviolet treatments. Usually, this process is considered lower temperature, i.e., ca. 80 °C, and treatment time of about 20 minutes.

Regardless of the considered encapsulant materials and adopted technologies for embedding the cells, the encapsulants must provide for PV modules mechanical stability, electrical safety and protection of the cells and other components from environmental impacts.

4. Additives for PV-module encapsulants

To achieve good stability and protection, the polymer-based encapsulants must be imperatively added with different additives that play different roles, for example: (i) crosslinking agents help the formation and structuration of 3D crosslinked sheets, [18–20] (ii) stabilizers, such as antioxidants, that prevent the thermal degradation of encapsulant materials during lamination process and in service, and UV absorbers and stabilizers, that protect the sheets against UV irrational in service conditions, [26,37,38] (iii) adhesion promoters ensure good adhesion between cells and other PV components. [61,62] All these additives have specific and unique tasks for the formulation and use of encapsulant materials in PV modules.

4.1. Crosslinking agents

The crosslinking agents, usually organic peroxides, help the formation and structuration of crosslinked encapsulants, improving the adhesion between the cells and other PV components and ensuring accurate isolation of PV modules by the environment. [18–20] As known, the formation of crosslinked structures is usually completed during the vacuum lamination process or roll-to-roll lamination process. Therefore, the formation of crosslinked structures proceeds by radical random reactions and its completion occurs upon heat of UV exposure.

4.2. Stabilizers: antioxidants and UV absorbers & stabilizers

Thermal stabilizers, such as phenolic antioxidant derivatives, are usually added to protect the polymer-based encapsulant against thermal degradation during prolonged lamination process and thermal shock in case of accidental "hot-spots" occurrence. [26] Unfortunately, the antioxidants being organic molecules, in the cases of hot-spots occurrence, they degrade and/or decompose quickly, and their degradation products could react with the degradation products of encapsulant sheets.

The addition of UV absorbers and stabilizers in the composition of encapsulant materials is absolutely imperative. As expected, the presence of both adsorbers and stabilizers helps to slow down the thermo-/photo- induced degradation of encapsulants through UV adsorption, radical capture and/or hydrogen donation. As known, the UV adsorbers are able to attract and adsorb the UV rays, transforming the energy in non-harmful energy, avoiding the macromolecule chain scission. The UV stabilizers have multi-functions, first, radical capture, and second, hydrogen donation, avoiding the propagation of radicals development upon UV rays. There are considered different UV stabilizers classes, such as classical benzophenones, hindered amines, etc, and all these additives do not change the encapsulant transparency and colour, and must be able to extend the life-time of encapsulants in service conditions.

4.3. Adhesion promoters

Adhesion promoters, usually based on silanes, help the adhesion and encapsulation of cells and other components. [61,62] The presence of adhesion promoters, unfortunately in some cases, could cause slight hazing of encapsulant and this could penalize the correct function of PV modules. Besides, occurring to the literature, silanes could catalyse the formation of acetic acid in EVA encapsulants leading to premature ribbons corrosion. Currently, the opportunity to replace the silanes-based adhesion promoters, by polar waxes containing different functional polar groups has been also proposed in the scientific literature. [62]

Summarizing all the above discussed considerations, the main advantages and disadvantages of different encapsulant additives are summarized in Table 3.

Table 3. Mostly considered additives of encapsulant materials for PV modules production and their main advantages and disadvantages.

Encapsulant additives	Advantages (+)	Disadvantages (-)
Crosslinkers	(+) formation of crosslinked structure fo the encapsulant materials	(-) not enough control of radical random crosslinking process
Antioxidants	(+) protection of encapsulants against thermal degradation during lamination and accidental hot-spots occurrence	(-) products of degradation of thermal stabilizers could react with other degradation by-products
UV absorbers and stabilizers	(+) protection of encapsulants against UV irradiation, slowing down the photoinduced degradation	(-) products of degradation of UV stabilizers could react with other degradation by-products
Adhesion promoters	(+) promotion of adhesion between the cells and other components	(-) could cause premature encapsulant hazing

5. Conclusions and future perspectives in module design

The PV modules development is related to the formulation of more and more performance devices with a power increase of more than 1%. Towards lither and low costs devices is the main direction for PV device development, and obviously, this requires more performance materials for next-generation PV modules.

Regarding the encapsulant materials, improving the UV cut-off to below 350 nm for PV encapsulant materials is absolutely desirable, and this could be obtained using specific additives ensuring cut-off effects.

Currently, the EVA is the most considered encapsulant, although it shows some drawbacks and the research for new encapsulants continues. EVA degradation pathways with the formation of acetic acids that cause ribbons corrosion to compromise the use of this encapsulant material. Nowadays, other encapsulants, based on TPO, POE, silicones and ionomers are also developed and all these materials show lower degradation tendency, in comparison to EVA, with less discolouration and opacity in service conditions. Therefore, encapsulants are very important components in PV modules production and assembly, and their failure could cause the failure of PV devices, significantly lowering the energy recovery and conversion.

To sum up, the research for novel encapsulants is related to the formulation of materials having favorable cost-performance balance, improved UV cut-off to below 350 nm and easy lamination process for PV-cells embedding, in terms of reduced curing times, lower process temperatures and pressures.

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