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What Is a Polyolefin? A Critical Overview of Ethylene Copolymers Used as Solar Photovoltaic Module Encapsulants

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ABSTRACT

In recent years, photovoltaic (PV) encapsulant films marketed as polyolefins (POs), more specifically as PO elastomers (POEs) and thermoplastic POs (TPOs), have gained significant market share and are projected to become the dominant encapsulation films by 2030. Relative to other industries, there are significant misconceptions about the term PO in the PV industry. Both in the scientific literature as well as in sales and advertising, the terms PO, POE, and TPO are often misused to describe the same type of material with comparable properties, while in reality these may each consist of separate material classes. This paper provides a comprehensive literature and market review, to showcase a broad range of PO and other ethylene copolymer encapsulants from recent studies, and discusses the materials' properties to clarify what constitutes a "polyolefin." In addition, to promote a clearer comparison of encapsulant properties, we propose a two-dimensional taxonomy to categorize polymers used in module manufacturing, including POs. In terms of improving the reliability of solar PV modules, PO-based encapsulants have several advantages (including lower water uptake and ion diffusion), but might come with disadvantages too, such as a more complex processing and a higher sensitivity to the storage conditions and shelf life. All this might prospectively impact adhesion properties of the encapsulant to other materials' interfaces (glass, cells etc.) and end-product quality. Because the track record of field-deployed PV modules containing PO encapsulants is also limited, we hope to contribute to better material understanding and precision in communication in PV to secure quality.

Abbreviations: AL-BSF, aluminum back surface field; ATR, attenuated total reflectance; CIGS, copper–indium–gallium–(di)selenide; DMA, dynamic mechanical analysis; DSC, differential scanning calorimetry; EBA, ethylene butyl acrylate; EEA, ethylene ethyl acrylate; EMA, ethylene-methyl acrylate; EPE, EVA/POE/EVA coextruded encapsulant films; EVA, poly(ethylene-co-vinyl acetate); FTIR, Fourier transform infrared spectroscopy; GMA, glycidyl methacrylate grafted; HDPE, high-density polyethylene; IEEE, Institute of Electrical and Electronics Engineers; LCOE, levelized cost of electricity; LDPE, low-density polyethylene; LLDPE, linear low-density polyethylene; MAH-g-POE, maleic anhydride grafted POE; MDPE, medium-density polyethylene; NREL, National Renewable Energy Laboratory; PBE, propylene-based elastomers; PDMS, polydimethylsiloxane; PERC, passivated emitter and rear contact; PID, potential-induced degradation; PID-s, PID by shunting; PMG, ethylene-methyl acrylate-glycidyl methacrylate terpolymer; PO, polyolefin; POE, polyolefin elastomers; POP, polyolefin plastomers; PP, polypropylene; PV, photovoltaic; PVB, polyvinyl butyral; PVF, polyvinyl fluoride; SHJ, silicon heterojunction; SPIE, Society of Photo-Optical Instrumentation Engineers; TOPcon, tunnel oxide passivated contact; TPO, thermoplastic polyolefin; TPU, thermoplastic urethane; ULDPE, ultra low-density polyethylene; UV, ultraviolet; UV-B, UV blocking; UV-T, UV transparent; VAc, vinyl acetate content; VIPV, vehicle-integrated photovoltaics; VLDPE, very low-density polyethylene; VTMS, ethylene/acrylate/vinyltrimethoxysilane; W, white; WVTR, water vapor transmission rate; α, hemispherical absorptance; ρ_δ, direct reflectance; ρ_η, hemispherical reflectance; τ_δ, direct transmittance; τ_η, hemispherical transmittance.

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1 | Introduction and Objectives

Following the invention of the first silicon-based solar cells in 1954, Bell Laboratories fabricated the first silicon PV module designed for outdoor applications in 1955. This initial module featured cells encapsulated in silicone oil within a plastic case. However, the outdoor exposure of the prototype was limited to just 5 months after its installation in 1956 [1].

Growing interest in re-evaluating terrestrial applications led to the release of small commercial modules by companies such as Sharp, Philips, and Solar Power in the early 1970s [1]. The subsequent oil embargoes and the use of photovoltaics in large professional telecommunication systems spurred the rapid development of module technology in the mid-1970s, with the first modern modules being fabricated in 1976. By the mid-1980s, almost all manufacturers had converged on a common module design. The general architecture of wafer-based crystalline silicon PV modules has been developed in the late 1970s and early 1980s within the Flat-Plate Solar Array Project and has not changed significantly [2]. Between 1980 and 1981, for the first time, poly(ethylene-co-vinyl acetate) (EVA) copolymer has been utilized as a solar cell encapsulant [1, 3]. Earlier encapsulation concepts included polydimethylsiloxane (PDMS) and polyvinyl butyral (PVB) [1,4].

A modern PV module consists of a number of strings of series-connected solar cells encapsulated into a single multi-layer composite. In most cases, it is surrounded by a frame providing the necessary structural support, usually also facilitating module mounting. The actual module has a layered encapsulation structure designed to protect the interconnected cells from the harsh outdoor environment. The primary purposes of this layout are mechanical and environmental protection, optical coupling, electrical insulation, and safety [4, 5]. In his historical overview of PV from 2005 onwards, Green explained that field experience over the last 20-plus years has demonstrated the inherent durability of the modern module design, stating also that this durability, however, comes with certain costs associated with the materials used, including tempered low-iron cover glass, EVA encapsulants, and Tedlar-based backsheets [1].

Since the late 1980s, chemically crosslinked EVA has become the dominant encapsulation material [6]. EVA is a random copolymer made from ethylene (E) and vinyl acetate (VA) monomers. In the PV industry, the copolymer consists of ethylene with about 28 wt.% (originally 33 wt.%) VA [4, 6, 7]. Solar grade EVA has melting temperatures between 60°C and 70°C and a glass transition temperature around −30°C, which—with PV module temperatures easily falling for clear sky days in the range between 45°C and 70°C—would therefore not fulfill the mechanical requirements for terrestrial PV applications [8]. However, by crosslinking the copolymer chains via the pressurized lamination process, the EVA sheet is transformed into a transparent, dimensionally stable encapsulant [9]. This crosslinking is initiated via a radical reaction, using an organic peroxide or peroxycarboxylic acid as a radical initiator [4, 7, 9]. The initial degree of crosslinking (after lamination typically in the range from 60% to 90%) is crucial as it both establishes strong interfacial adhesion and sets the long-term characteristics of the material and is therefore highly relevant for the quality and long-term stability of the produced PV module [10–12]. EVA obtained its market leadership due to its mechanical flexibility, transparency, good processability, and cost-effectiveness. Moreover, it has over 40 years of experience in production and field life and is therefore perceived as a reliable encapsulant material. Some limitations, however, are present too. EVA requires chemical crosslinking for thermo-mechanical stability; therefore, it has a limited shelf life, a time and energy-intensive lamination process, and can upon exposure to UV and humidity form acetic acid as a degradation byproduct. Acetic acid is among others linked to several PV module failure mechanisms like corrosion of cell metallization and interconnections, delamination, potential induced degradation, encapsulant oxidation and yellowing [7, 10, 13]. Despite these challenges, its benefits made it a popular choice for encapsulation of PV modules, ensuring adequate durability and performance. It is forecasted that the market share of EVA encapsulants will fall below 50% by 2030, with so-called polyolefins (POs) and EVA/POE mixtures becoming the most used encapsulants (Figure 1). The remaining encapsulants, categorized as "others," include PVB, polyurethane, and silicone-based material [14, 15].

Research on POs as alternative non-EVA encapsulant started in the mid to late 1990s. Between 1995 and 1997, Evergreen Solar was working on the development of an alternative encapsulant. The two main motivations were to find an encapsulant with process advantages—in particular, one that could be laminated in air, and better product performance, particularly UV stability [16]. Pern and Glick investigated the degradation behavior of encapsulated Si solar cells with accelerated aging tests, also using the thermoplastic PO (TPO)-based encapsulant from Evergreen Solar [17]. The authors concluded that the new PO encapsulant may avoid adhesion failure and be a suitable encapsulant if the modules are not used at high operating temperatures [18]. The same group of authors mentioned a polyethylene thermoset adhesive for encapsulation in April 2000 [19]. However, no other information was given regarding the encapsulant.

Research on ionomers as solar cell encapsulants started in the early 2000s. In 2005, Dupont filed a patent for multilayer ionomer films for use as encapsulant layers for solar cells [20]. Ionomers

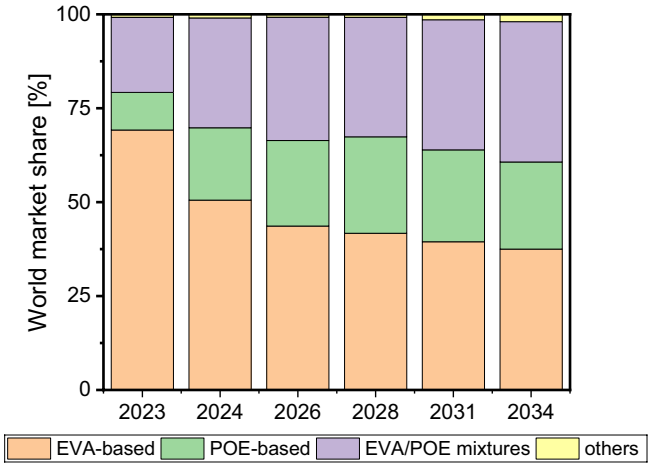

FIGURE 1 | Current encapsulant market share and forecast until 2034 [14].

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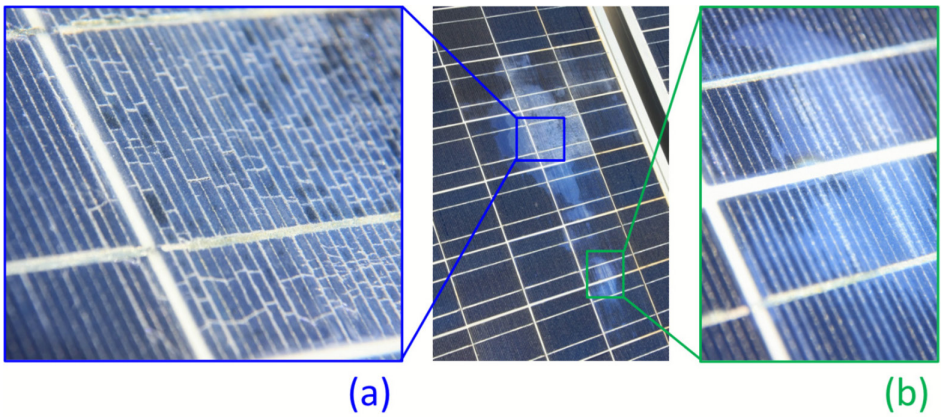

FIGURE 2 | Visual appearance of a PV module using an ionomer encapsulant after 12 years in Tucson, AZ, USA. Details of (a) cracking and (b) delamination are shown in the insets.

are copolymers of ethylene and acid comonomers such as methacrylic acid or acrylic acid, subsequently neutralized with metal ions, like sodium or zinc [21, 22]. Ionomers are frequently noted for their low water vapor transmission rates (WVTRs) and minimal water absorption, making them effective in protecting PV modules from corrosion and moisture-related degradation [23–27]. Hence, they were first investigated as encapsulants for moisture-sensitive thin film solar cells like copper–indium–gallium–(di)selenide (CIGS), amorphous silicon, or amorphous/micromorph silicon tandem cells [26–32]. Ionomers have also been investigated for their use in low concentrator PV modules [33–35]. Compared with modules with EVA, they also show higher resistance to potential-induced degradation (PID) [26, 28, 36, 37] and corrosion of transparent conductive electrodes [38]. However, ionomers have higher mechanical stiffness [29], and therefore face challenges with delamination issues over time [21, 22]. Figure 2 shows an example of an early formulation of ionomer, where both delamination and cracking of the material were observed at two separate sites in Arizona. Degradation was most often observed proximate to the junction box (an area of the module that tends to overheat) [39, 40]. Only modules manufactured between January 2001 and September 2001 were affected. Proper industry feedback led to improved formulations, apparently solving the problem.

In 2006, Pern described unsatisfactory results of his investigation of low-cost PO films, highlighting their inadequate adhesion strength. He concluded that as of August 2006 the use of PO encapsulants in commercial products may not be appropriate [41]. The US National Renewable Energy Laboratory (NREL) developed and tested a so-called PMG, which is an ethylene-methyl acrylate-glycidyl methacrylate terpolymer. While PMG has a slightly higher raw resin cost compared with EVA, its fabrication and use as extruded films are similar. NREL's PMG formulations demonstrated excellent photostability, high adhesion strength to glass, and superior resistance to damp heat exposure [41]. However, despite its excellent properties, for reasons not known to the authors, the material has never been commercialized for use in PV modules.

In 2008, the Dow Chemical Company presented work on functionalized PO materials for PV encapsulation. The materials provided reduced moisture permeation, eliminated the need for curing, and did not produce acetic acid. These properties reduce process cycle time and limit the risk of subsequent corrosion damage. The POs were also lower density than EVA and maintained better adhesion to glass under varying temperature and humidity conditions [42].

In 2009, Oreski and Wallner investigated ethylene copolymers based on α-olefins, acrylic acids and acrylates as potential solar cell encapsulants [43, 44]. The investigated copolymers, with comonomer contents of about 10% offered similar or better mechanical and optical properties than EVA. Interestingly, one of the polymers in this study, ethylene-methyl acrylate (EMA), had already been investigated in the Flat-Plate Solar Array project for its suitability as solar cell encapsulants [3, 45, 46]. This approach however was not pursued further in favor of EVA [45, 46].

From 2010 onwards, the development of new ethylene copolymer-based materials has driven the interest towards the replacement of EVA. Various types of encapsulation films have been introduced and investigated since then under the label "polyolefin encapsulants" [47–110] that garnered a market share approaching 20% in 2024 [15].

In 2020, Patel et al. [111] concluded that EVA might have been a good encapsulant for glass-backsheet modules over the decades, but it may prove to be an inappropriate choice for double glass modules [15]. Evidence supporting this conclusion includes severe encapsulant browning, acetic acid formation, and interconnect corrosion observed in fielded bifacial modules—all issues related to the presence of EVA in less-permeable module structures. They concluded that ionomers or PO-based encapsulants could be better suited for application in double glass modules. Despite these limitations, attempts to use EVA in glass/glass structures have given encouraging results in the lab—provided an extremely careful storage in a moisture-free environment is used before the lamination [112].

Recent material innovations tend to be classified as PO encapsulants, as cross-linked PO elastomers (POEs) or TPO encapsulants. The main motivations for the use of new non-EVA encapsulants have been:

- Reduced corrosion [48, 56, 58, 59, 84, 90, 96]
- Reduced PID-risk and ion diffusion [61, 62, 76, 113–115]

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- Reduced discoloration [56, 77]
- Enhanced compatibility with new cell/interconnection technologies [79, 91–93, 116–120]
- Modules for specific applications or environmental conditions [87, 104, 121–124]
- Encapsulation of perovskite or perovskite tandem solar cells [99, 125–130].

The new PO-based materials caught the attention of the academic and industrial sectors, but more studies are necessary—long-term indoor and outdoor exposure investigations are especially crucial to discover new degradation modes that might appear [121]. Additionally, the effects of the long-term interaction between the new encapsulation materials and the other module components are not known. More importantly, even though PO based encapsulants are used by various module manufacturers since more than a decade, one example being First Solar [131], no comprehensive investigation on the long-term outdoor behavior of these encapsulants have been published yet. In comparison, published field studies for modules using EVA or PVB encapsulants extend over 40 years [6, 7].

Unfortunately, the terms PO, POE, or TPO are used in a manner that implies that all POE or TPO encapsulants are the same. Additionally, the term "polyolefin" is understood differently in PV applications relative to other industries and polymer science. Elsewhere, PO refers to any of a class of polymers produced from simple olefins (i.e., an alkene with the general formula C_nH_{2n} as monomers [132]). That includes thermoplastics like polyethylene and polypropylene (PP), but also POEs such as polyisobutylene or ethylene propylene rubbers. The introduction of diene monomers, such as butadiene and isoprene, however, yields polymers that are not referred to in the PV industry as a "polyolefin." The PV technical community, historically lacking polymer science expertise, often incorrectly used the terms "polyolefin" and "POE" to refer to any encapsulant comprising ethylene polymers other than EVA. These may also contain other functional groups such as acrylates or acrylic acids not universally classified as a "polyolefin."

This article aims to give an overview of state-of-the-art knowledge on "polyolefin" encapsulation materials and how variations in the composition, curing mechanisms, and processing conditions of PO-based encapsulants impact the long-term reliability and performance of PV modules compared with EVA encapsulants. For this review paper, we have conducted a comprehensive exploration of existing literature published over the past 50 years that mention PO-based encapsulants. Moreover, we collected and summarized information on 74 different PO-based encapsulants that have been investigated by the authors over the last 20 years. We intend this article to serve as a compact and topical introduction to this topic for specialists in PV technology and reliability, as well as for newcomers entering the field of PV reliability engineering.

Starting from the historical overview of PO encapsulant development in Section 1, Section 2 will establish a taxonomy of ethylene copolymer encapsulants, present statistical insights into past research, and analyze the chemical structures and properties of various PO-based films used in PV modules. Section 3 will detail the key physical, chemical, and mechanical properties of PO encapsulants. Section 4 will assess the performance of ethylene copolymer-based encapsulants, particularly their effects on module lamination and overall efficiency. Degradation mechanisms such as delamination, PID, and corrosion will be examined in relation to encapsulant properties. Section 5 will present a comparative discussion on PO-based encapsulants versus traditional EVA, evaluating long-term durability, processing efficiency, and overall PV module performance. Manufacturing aspects, field reliability, and challenges in comparing published results will be discussed.

Finally, Section 6 will summarize key findings, emphasizing the need for more precise classification of PO encapsulants and highlighting critical gaps in current research that must be addressed for the advancement of PV module reliability.

2 | Market and Literature Survey on Ethylene Copolymers

2.1 | Taxonomy of Ethylene Copolymer Encapsulants

Encapsulants can be categorized using two dimensions: (1) the identity of the base resin used to make the encapsulant film; and (2) the nature of the film during lamination (i.e., curing vs. noncuring). At times, encapsulants have been categorized by only one of these two dimensions, leading to confusion.

Figure 3 provides a taxonomy for common polymers used in PV encapsulation, focusing on ethylene polymers. Three primary subcategories of ethylene polymers are presented. POs and ethylene/polar copolymers are each reactor product subcategories. The third subcategory is for polymers from either reactor subcategory that have been further modified to provide additional functionality. From a polymer resin perspective, PO and TPO are comparable terms. All of the polymers listed in the blue box in Figure 3 are POs and are TPOs. The TPO acronym is used in many industries, often imprecisely and/or inaccurately. For example, in the automotive industry, TPOs generally refer to blends of PP and POEs (ethylene/α-olefin copolymers) and optionally talc. Similarly, TPO PV backsheets can be based on PP or PP/POE blends [133–136]. Meanwhile, TPO encapsulants have at times referred to encapsulants that do not cure during lamination, which is a characteristic of the 2nd categorization dimension highlighted below, rather than a characteristic of the base resin. Also note that from a polymer resin perspective, POEs are a subset of PO or TPO resins. The term POE is also broad. In most industries, including PV encapsulants, POEs are more precisely ethylene/α-olefin copolymers, such as ethylene/propylene, ethylene/butene, and ethylene/octene copolymers. Furthermore, they are a subset of ethylene/α-olefin copolymers with high comonomer content and density less than about 0.90 g/cm^3. The term POE also includes propylene/ethylene copolymers, where propylene is the majority monomer. These are also technically POEs, but are often referred to as propylene-based elastomers (PBEs) to distinguish them from ethylene/α-olefin POEs. PBEs are not widely used as PV encapsulants because of their higher modulus and difficulty to crosslink using peroxides. EVA is an ethylene/polar copolymer made in a free radical reaction under high pressure. Several other ethylene/polar copolymer

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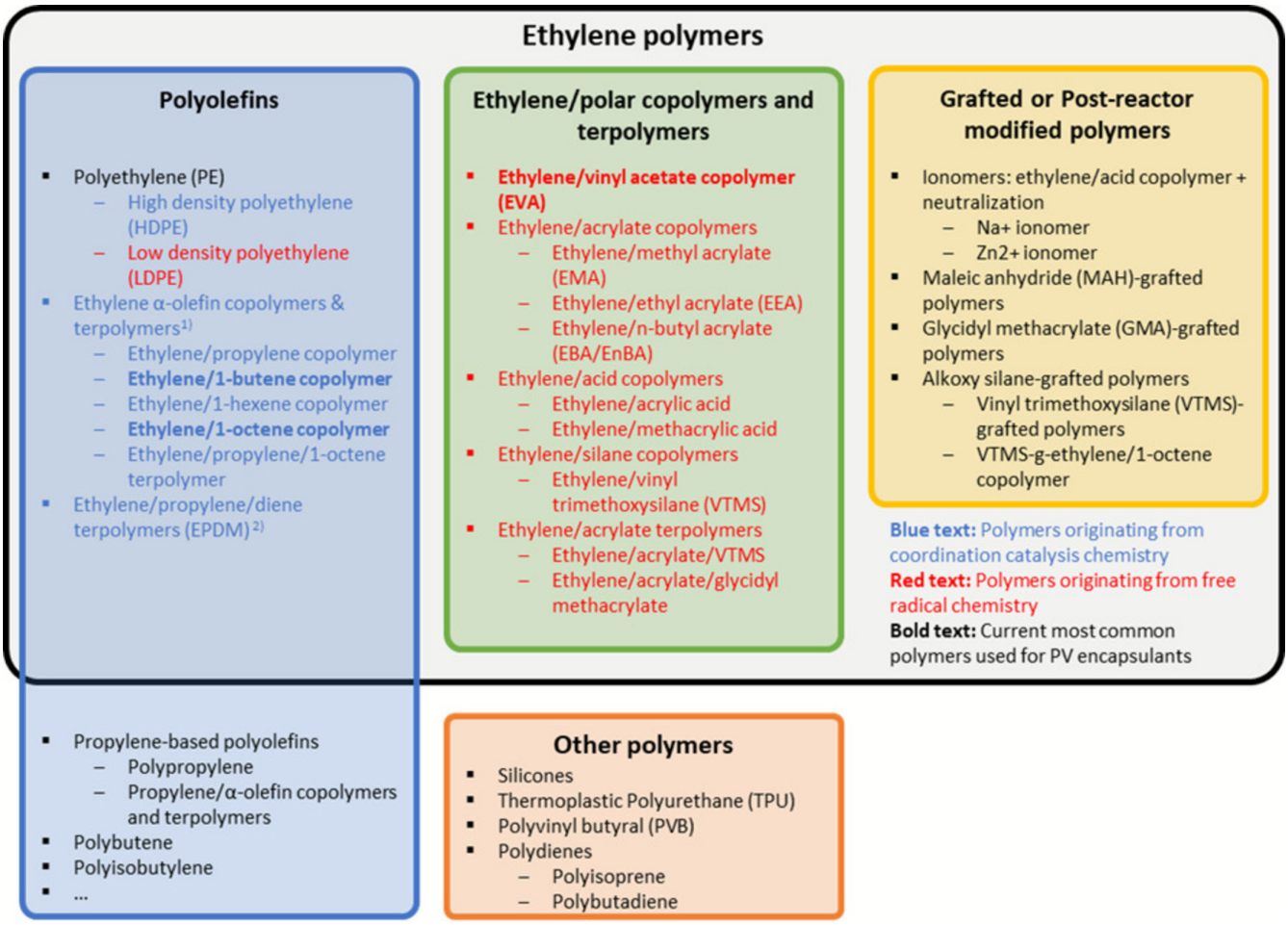

FIGURE 3 | Encapsulant resin taxonomy—the families of ethylene copolymers. List represents some of the most common commercially relevant polymers. [1]Subclasses often defined in the industry by density ranges, which can overlap. From highest to lowest density: high-density polyethylene (HDPE); medium-density polyethylene (MDPE); linear low-density polyethylene (LLDPE); very low-density polyethylene (VLDPE); ultra low-density polyethylene (ULDPE); polyolefin plastomers (POPs); polyolefin elastomers (POEs). [2]Do not meet the strict definition of a polyolefin as they contain dienes, but are often grouped with polyolefins as the diene content is low (generally < 10 wt.%).

and terpolymer resins have been used in PV encapsulants, including ethylene/acrylate copolymers and ethylene/acrylate/vinyltrimethoxysilane (VTMS) terpolymers. Post-reactor modified polyethylene copolymers are polyethylene-based materials chemically altered after polymerization by grafting functional groups such as maleic anhydride (MAH), glycidyl methacrylate (GMA), or alkoxy silanes. The main purpose of the grafted functional groups is to provide adhesion to glass and the silicon solar cells. Enhanced adhesion in post-reactor modified polyethylene copolymers primarily stems from the introduction of polar functional groups onto the non-polar polyethylene backbone. These grafted groups, like MAH, GMA, or alkoxy silanes, provide reactive sites that can form strong chemical bonds (covalent bonds) or robust intermolecular interactions (e.g., hydrogen bonding, dipole–dipole interactions) with polar surfaces such as glass or other module materials [137].

Figure 4 provides a description of the 2nd categorization dimension based on the structure of the encapsulant films, lamination and subsequent use. All encapsulation films are thermoplastic as produced. The majority of encapsulant films today can be classified as cured encapsulants, which are designed to crosslink into a thermoset during lamination. The second sub-category is non-cured encapsulants, which confusingly have sometimes been referred to as "TPO" encapsulants, which are designed to remain thermoplastic during lamination of the modules. This subcategory can be further divided into two groups: latent cured films that can crosslink over time after production; and thermoplastic encapsulants that do not crosslink but remain thermoplastic over the lifetime of a PV module. The degree of crosslinking achieved in the latent cure encapsulants may not be as high as in the cured encapsulants because for the non-cured subcategory (both latent cure and thermoplastic) the required thermal stability is provided by the crystallinity of the resin [138]. Many ethylene-based encapsulants will cross-link over time in fielded PV modules as a result of degradation due to typical operating conditions.

2.2 | Literature Overview: Statistics and Research Topics

A comprehensive literature review identified 228 scientific and technical publications describing PO or ethylene copolymer-based encapsulants. In addition to journal articles, relevant indexed conference contributions (European Photovoltaic Solar

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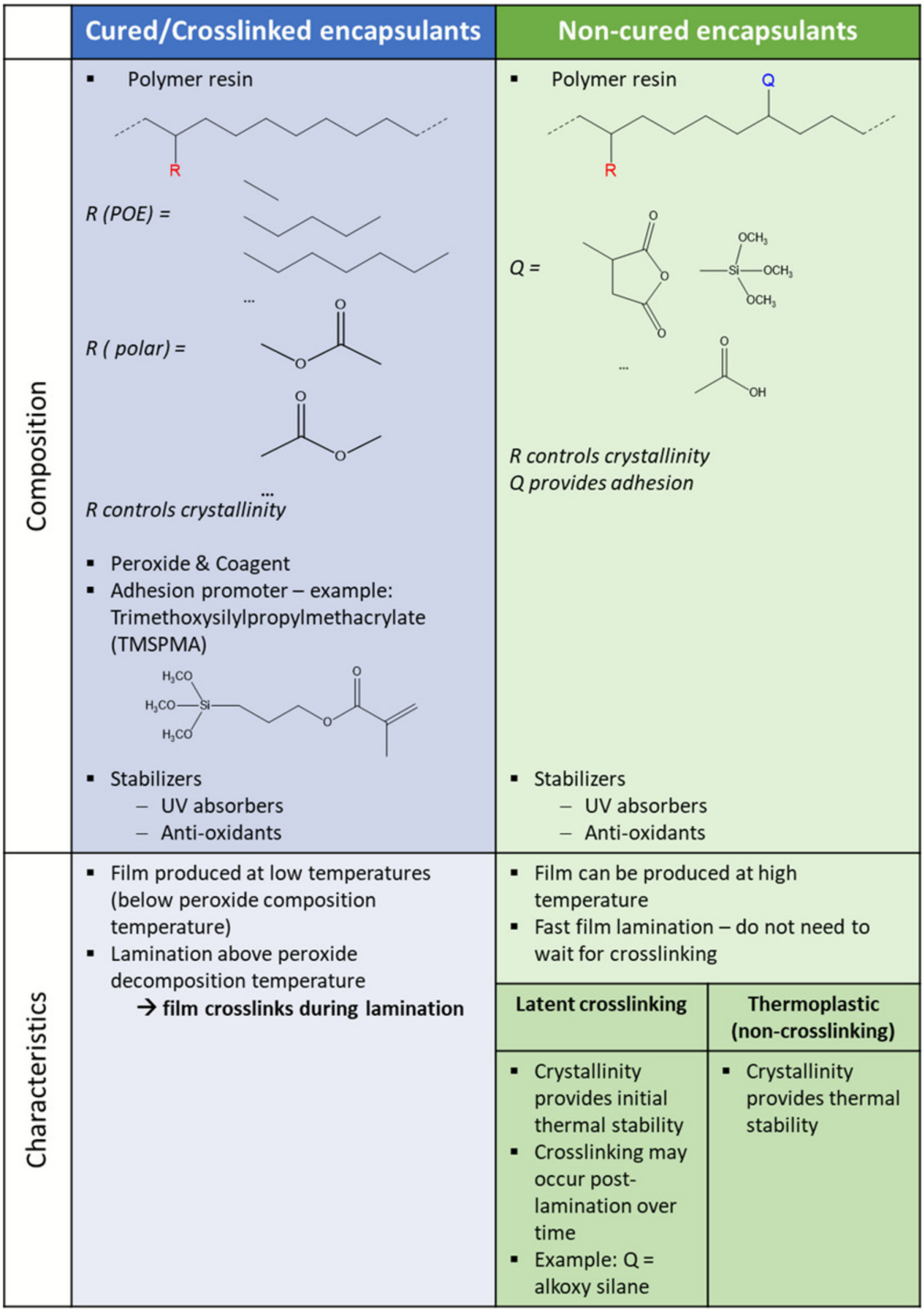

FIGURE 4 | Encapsulant film taxonomy—including structure, lamination, and subsequent use.

Energy Conference, IEEE Photovoltaic Specialists Conference, SPIE Optics & Photonics) and indexed technical reports were considered. The full list of publications can be found in Tables S1 and S2. For each publication, the following information was systematically recorded (see Table S2):

- Type and year of publication (see Figure 5)
- Number and type of investigated materials (Ionomer, POE, TPO, or PO; see Figures 6 and 7
- If mentioned, chemical composition and manufacturer of the encapsulation material
- Main topics(s) that were classified under 12 categories (Figure 8)

Overall, 391 encapsulant films have been reported with particular emphasis on POE (152 mentions) and TPO (113 mentions). Just "polyolefin" is reported 53 times, where until 2010, no other relevant information such as polymer resin type or the use of

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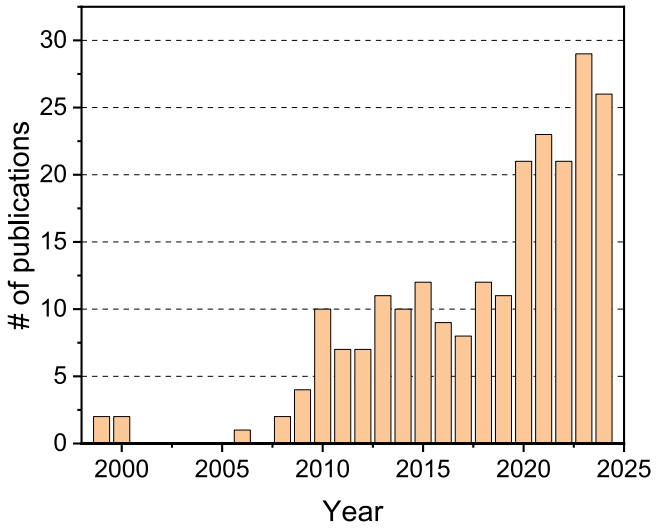

FIGURE 5 | Number of papers investigating ethylene copolymer based encapsulants (alternative to EVA) for PV modules per year.

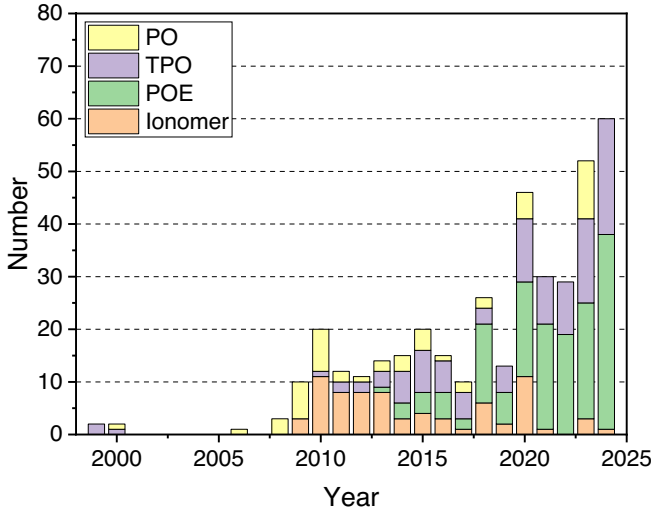

FIGURE 6 | Number of mentions of ethylene copolymer based encapsulants in publications (alternative to EVA) for PV modules per year.

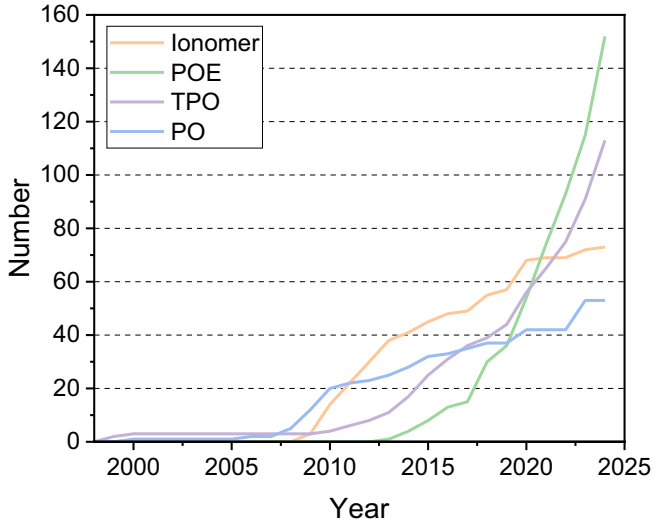

FIGURE 7 | Cumulative number of mentions of ethylene copolymer based encapsulants (alternative to EVA) for PV modules.

a crosslinking agent is specified. Ionomer encapsulation materials were mentioned 73 times. To give some perspective, by comparison, a quick literature research on EVA encapsulant for PV modules delivered more than 1200 publications for the same time period.

Very few publications discuss alternatives to EVA before 2009 and they mostly deal with material development and characterization. A significant increase in research publications (to approximately 10 per year) is observed from 2010 to 2019. Within this decade, ionomers have been the most investigated non-EVA encapsulant. One factor was the interest in using ionomers for special applications like thin film modules [26, 28] or concentrator PV [35]. Another, possibly stronger driver was the increased incidence of PID [114]. Replacing EVA with ionomers or POs was found to be a successful PID mitigation strategy [36, 90].

Another significant increase in published research was seen from 2020 to 2024, with 20–30 publications per year. This coincides with the shift of the PV industry towards double glass modules. Within the last 5 years encapsulant films labeled as POE or TPO also superseded ionomers as the most studied materials. The main driving research topics have been compatibility with new cell technologies like *passivated emitter and rear contact* (PERC) [48, 76], *silicon heterojunction* (SHJ) [62, 91, 120], *tunnel oxide passivated contact* (TOPCon) [119], or perovskites [125, 128].

While some topics are peaking within a certain time period, other topics occur consistently over the last 15 years. Some examples are material development and material characterization, optical properties, adhesion, and thermo-mechanical behavior. There are also comparatively regular publications on the subject of modules for special applications or climatic conditions. Within that category light-weight PV [124], concentrator PV [35] or modules for desert climates [121, 139] have been investigated. Finally, publications dealing with process optimization and investigation of the curing behavior of PO encapsulants [65, 67] as well as sustainability and recycling [86] appear more recently, with nearly all publications occurring between 2019 and 2024.

Information about manufacturers and chemical structures is not consistently listed. Out of 391 investigated encapsulant films, the manufacturer is listed for 62 materials, and only in 45 cases is information given on the chemical composition of the encapsulant film.

2.3 | Identification and Examination of Chemical Structure and Properties of Different PO Based Encapsulant Films

Table 1 provides a summary of the ethylene copolymer based encapsulants that have been collected and characterized by the institutions and companies contributing to this publication. It includes 74 different types from at least 26 different manufacturers as of November 2024. This compilation does not aim to cover the entire past or current market of "polyolefin" encapsulants. Instead, it focuses exclusively on materials that have been

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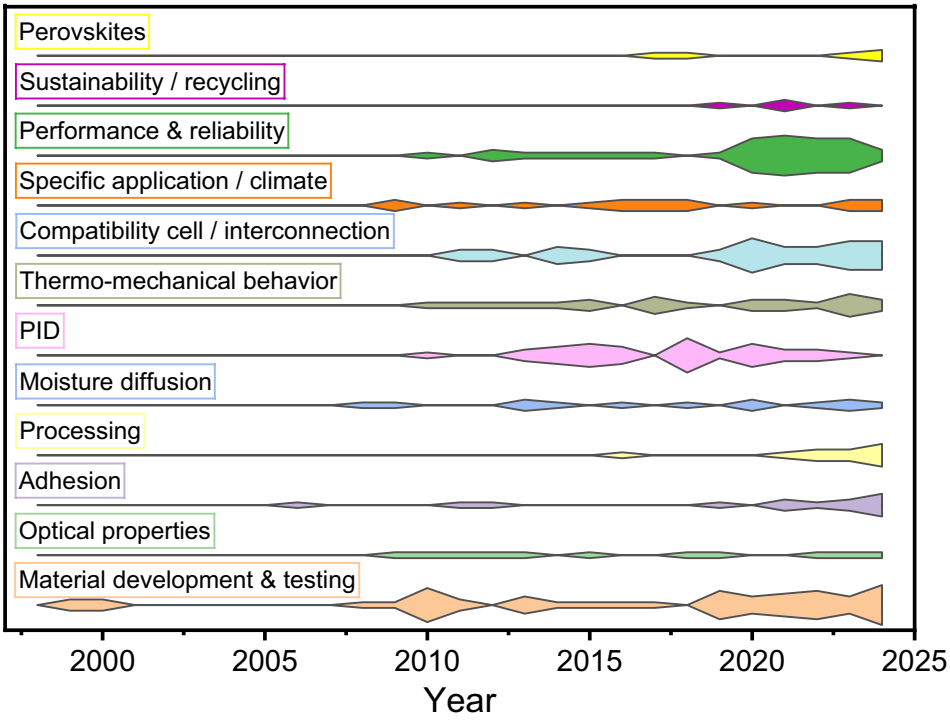

FIGURE 8 | Distribution of main research topics related to ethylene copolymer encapsulant films.

verified and characterized by the authors over the last 20 years, to identify and classify the relevant compositions of commercial and research products. However, to the best of the authors' knowledge, almost all relevant products from current market players are included in the table, [140], as well as from previous market leaders and early innovators.

The encapsulant films listed in Table 1 were investigated between 2006 and 2024. The year given in the table is the year the encapsulant film was obtained and characterized by the respective partner, and not the production date of the film. Due to the nearly two-decade span of this investigation, not all the commercial films are currently available for purchase. Some were developmental samples that were never released to the market, while others are no longer available due to the cancellation of product lines or companies exiting the industry. In some cases, encapsulant films with the same brand name have been investigated several times by multiple partners over the years. For some materials, multiple development versions have been investigated. All these versions are listed under the same sample number with suffixes starting from lower case a.

The chemical structure of materials can be characterized by means of Fourier transform infrared (FTIR) spectroscopy in attenuated total reflectance (ATR) mode [141]. Five different base polymers were identified among the monolayer encapsulants tested, as seen in Figure 9. The polymers have the typical peaks of polyethylene in common as can be seen from the bands at about 2916, 2849, 1464, and 719 cm^{-1} corresponding to the asymmetric and symmetric stretching vibrations of CH_2, asymmetric deformation vibration of CH_2 and skeletal rocking vibrations of CH_2, respectively [143].

Copolymers of ethylene and butyl or ethyl acrylate additionally show bands at 1733 and 1164 cm^{-1}, corresponding to C=O (ester group) and C–O–C stretching vibrations, respectively [43, 48]. Ethylene acrylic acid copolymers have a characteristic band at about 1698 cm^{-1} that can be attributed to C=O stretching vibrations of the carboxyl group [144].

The intensity and the shape of the bands can vary depending on the ratio between ethylene, α-olefin comonomers, and polar comonomers and the polymerization process. Furthermore, even within the same polymer composition type, it is possible to notice that there are detectable differences, mostly due to additive formulations as well as fillers and pigments.

Melting temperature as well as the confirmation of peroxide induced crosslinking was determined using differential scanning calorimetry (DSC). Figure 10 shows the distribution of melting temperatures of the tested encapsulants in Table 1. Recorded melting peak temperatures range from a minimum of 49°C to a maximum of 121°C. Be aware, the distribution shown in Figure 10 is not representative of the market, as it consists exclusively of materials that have been verified and characterized by the authors over the last 20 years. For example, due to specific research work by the partners, encapsulants with melting temperatures between 90°C and 110°C are over-represented in this figure.

Melting temperatures well below 120°C suggest that many of the studied encapsulants are copolymers of ethylene and α-olefin, where the amount of co-polymerized side groups is decreasing the melting temperature as well as the degree of crystallinity [145, 146]. Melting temperatures in the range of 100°C–120°C can also be associated with low-density polyethylene (LDPE), which does not contain α-olefin comonomer, but has a high degree of long chain branching as well as short, typically 4-carbon branches.

Regarding materials collected from the same manufacturer and with the same commercial name, but produced in different

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TABLE 1 | List of ethylene copolymer based encapsulants that have been collected and characterized by the institutions and companies contributing to this publication: The table contains melting temperature and information on the curing chemistry (peroxide, silane, none), the optical properties (UV transparent [UV-T]; UV blocking [UV-B]; and white [W]), and the availability of the encapsulant in November 2024. Field are marked with N.A., in case the specific information was not obtainable anymore.

Film #	Sample #	Manufacturer	Material composition	Melting temperature [°C]	Curing chemistry	Optical properties	Year of investigation	Availability 2024
1	1	M1	Ethylene butyl acrylate	81	Peroxide	UV-T	2015	No
2	2	M1	Ethylene butyl acrylate	80	Peroxide	UV-T	2015	No
3	3	M1	Ethylene butyl acrylate	90	Peroxide	UV-B	2021	No
4	4a	M2	Ethylene ethyl acrylate/VTMS	91	Silane	W	2019	No
5	4b	M2	Ethylene ethyl acrylate/VTMS	91	Silane	UV-T	2019	
6	4c	M2	Ethylene ethyl acrylate/VTMS	93	Silane	UV-T	2020	
7	4d	M2	Ethylene ethyl acrylate/VTMS	92	Silane	W	2020	
8	4e	M2	Ethylene ethyl acrylate/VTMS	91	Silane	UV-T	2021	
9	4f	M2	Ethylene ethyl acrylate/VTMS	92	Silane	UV-B	2021	
10	4g	M2	Ethylene ethyl acrylate/VTMS	92	Silane	UV-T	2023	
11	4h	M2	Ethylene ethyl acrylate/VTMS	92	Silane	UV-B	2023	
12	5	M3	Ethylene α-olefin	62	Peroxide	UV-T	2018	Yes
13	6a	M4	Ethylene α-olefin	66	Peroxide	UV-T	2018	Yes
14	6b	M4	Ethylene α-olefin	69	Peroxide	UV-T	2022	
15	6c	M4	Ethylene α-olefin	60	Peroxide	UV-T	2023	
16	6d	M4	Ethylene α-olefin	65	Peroxide	UV-T	2023	
17	7a	M4	Ethylene α-olefin	72	Peroxide	UV-B	2022	Yes
18	7b	M4	Ethylene α-olefin	69	Peroxide	UV-B	2023	

(Continues)

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TABLE 1 | (Continued)

Film #	Sample #	Manufacturer	Material composition	Melting temperature [°C]	Curing chemistry	Optical properties	Year of investigation	Availability 2024
19	8a	M4	Ethylene α-olefin	104	Peroxide	UV-T	2022	No
20	8b	M4	Ethylene α-olefin	103	Peroxide	UV-T	2023	
21	9	M4	Ethylene α-olefin	65	Peroxide	UV-T	2022	No
22	10	M4	Ethylene α-olefin	95	Peroxide	UV-T	2022	No
23	11a	M5	Ethylene α-olefin	54	Peroxide	UV-T	2018	Yes
24	11b	M5	Ethylene α-olefin	54	Peroxide	UV-T	2023	
25	12a	M5	Ethylene α-olefin	55	Peroxide	UV-B	2023	Yes
26	12b	M5	Ethylene α-olefin	55	Peroxide	UV-B	2021	
27	13	M5	Ethylene α-olefin	55	Peroxide	UV-T	2023	Yes
28	14a	M6	Ethylene α-olefin	71	Peroxide	UV-T	2018	Yes
29	14b	M6	Ethylene α-olefin	63	Peroxide	UV-T	2022	Yes
30	15a	M6	Ethylene α-olefin	64	Peroxide	UV-B	2022	Yes
31	15b	M6	Ethylene α-olefin	62	Peroxide	UV-B	2023	Yes
32	16	M7	Ethylene α-olefin	75; 110	None	UV-T	2018	No
33	17	M7	Ethylene α-olefin	54; 113	None	UV-B	2018	No
34	18	M8	Ethylene acrylic acid	90	None	UV-B	2010	No
35	19	M8	Ethylene acrylic acid/ butyl acrylate	97	None	UV-B	2010	No
36	20	M9	Ethylene α-olefin	92	None	UV-T	2010	No
37	21	M9	Ethylene α-olefin	103	None	UV-T	2023	Yes
38	22	M10	Ethylene α-olefin	61; 121	Silane	UV-T	2021	Yes
39	23	M10	Ethylene α-olefin	121	Silane	N.A.	2023	Yes
40	24	M11	Ethylene α-olefin	74	Peroxide	UV-B	2021	Yes
41	25	M12	Ethylene acrylic acid	93	None	UV-T	2021	No
42	26	M13	Ethylene/ethyl acrylate/VTMS	90	Silane	UV-T	2024	Yes

(Continues)

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TABLE 1 | (Continued)

Film #	Sample #	Manufacturer	Material composition	Melting temperature [°C]	Curing chemistry	Optical properties	Year of investigation	Availability 2024
43	27	M14	Ethylene α-olefin	64	Peroxide	UV-T	2022	Yes
44	28	M14	Ethylene α-olefin	64	Peroxide	UV-B	2022	Yes
45	29	M15	Ethylene ethyl acrylate/VTMS	91	Silane	UV-B	2022	Yes
46	30	M15	Ethylene α-olefin	60	Peroxide	UV-T	2022	Yes
47	31a	M15	Ethylene α-olefin	49	Peroxide	UV-T	2022	Yes
48	31b	M15	Ethylene α-olefin	49	Peroxide	UV-B	2022	Yes
49	32	M16	Ethylene α-olefin	52	Peroxide	UV-T	2022	Yes
50	33a	M16	Ethylene α-olefin	75	Peroxide	UV-B	2023	Yes
51	33b	M16	Ethylene α-olefin	75	Peroxide	UV-B	2023	Yes
52	33c	M16	Ethylene α-olefin	72	Peroxide	UV-B	2023	Yes
53	34a	M16	Ethylene α-olefin	74	None	N.A.	2023	No
54	34b	M16	Ethylene α-olefin	72	None	N.A.	2023	No
55	35a	M16	Ethylene α-olefin	71	None	UV-B	2023	No
56	35b	M16	Ethylene α-olefin	73	None	UV-B	2023	No
57	35c	M16	Ethylene α-olefin	64	None	UV-B	2023	No
58	35d	M16	Ethylene α-olefin	102	None	UV-T	2023	No
59	36a	M17	Ethylene α-olefin	76	Peroxide	UV-B	2022	Yes
60	36b	M17	Ethylene α-olefin	76	Peroxide	UV-T	2022	Yes
61	37	M18	Ethylene α-olefin	95	None	UV-T	2017	No
62	38	N.A.	Ethylene α-olefin	77	None	UV-B	2017	N.A.
63	39	M19	Ethylene α-olefin	82	None	UV-B	2011	N.A.
64	40	M19	Ethylene α-olefin	102	None	UV-B	2011	N.A.
65	41	M20	Ethylene α-olefin	95	None	UV-B	2011	N.A.
66	42	M21	Ethylene-octene	62	Peroxide	UV-B	2007	No
67	43	M22	Ethylene acrylic acid	84	None	UV-B	2011	No

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TABLE 1 | (Continued)

Film #	Sample #	Manufacturer	Material composition	Melting temperature [°C]	Curing chemistry	Optical properties	Year of investigation	Availability 2024
68	44	M23	Ethylene acrylic acid/polyamide	84; 128	None	UV-B	2011	No
69	45	N.A.	Ethylene α-olefin	63	Peroxide	UV-T	2022	N.A.
70	46	N.A.	Ethylene α-olefin	67	Peroxide	UV-T	2024	N.A.
71	47	M24	Ethylene butyl acrylate	92	Peroxide	UV-T	2023	Yes
72	48	M25	Ethylene α-olefin	59	Peroxide	UV-T	2024	Yes
73	49	M26	Ethylene alpha olefin/acrylic acid	62	Peroxide	UV-T	2024	Yes
74	50	M26	Ethylene alpha olefin/acrylic acid	62	Peroxide	UV-B	2024	Yes

Note: The background is alternating between blue and white based on the manufacturer of the encapsulant.

years, we observed variation in melting temperature (obtained from the 2nd heating step) over the years. For samples 6a to 6d, which are ethylene/α-olefin based and have been investigated between 2018 and 2023, the melting temperature ranges from 60°C to 69°C. This difference indicates variations in the co-monomer content or type of the base polymer (propylene, butene, and octene) [147]. Similar observations have been made for encapsulant film numbers 14a and 14b (sourced in 2018 and 2022), with melting temperatures of 63°C and 71°C, respectively.

An exothermic peak around ~160°C forms upon heating during DSC of some encapsulants, and corresponds to the decomposition reaction of peroxides during crosslinking. However, DSC alone is not sufficient to measure the degree of cross-linking because the shape of the peak is influenced by (i) the type of the chemical system that initiates the crosslinking reaction, (ii) the heating rate, and (iii) the presence of stabilizers that might interact with synergistic or antagonistic effects relative to the crosslinking process [148]. To better assess the crosslinking behavior of polymers, DSC measurements should be compared with changes in the rheological properties of the polymer or Soxhlet extraction [149]. Change in viscosity corresponds to the formation of links between the polymer chains, resulting in a reduction in mobility [11].

PO encapsulants with two different curing chemistries have been identified. Peroxide crosslinked encapsulants have been developed in the 1980s and are widely used in the solar industry due to their excellent balance of mechanical flexibility, adhesion, and protective properties [3, 4]. Crosslinking is crucial for ensuring the long-term efficiency and performance of PV modules [4, 9, 11, 12, 150]. Hence, peroxide curing is used not only for EVA but also for most POE-based encapsulation materials, as shown in Table 1. For peroxide-initiated cross-linking, water is avoided in storage and lamination because it compromises the alkoxysilane adhesion promoter used in the film composition [112, 151].

Recent encapsulant film developments exploit a different curing chemistry based on incorporating alkoxysilane functionality (often referred to more simply as silane) onto the polymer itself, as opposed to small molecule alkoxysilanes that are included in peroxide-cured encapsulants but not bonded to the polymer backbone prior to lamination [98]. Alkoxysilane moisture curing of polyethylene (copolymers) is a 30-year established technology and is mainly used for polymer pipes and cable sheathing [152–154]. In PV modules, crosslinking of silane-grafted encapsulant films happens in the first few weeks after production, so any modules with this chemistry must pass qualification testing without necessarily having been crosslinked [155].

3 | Properties of PO Encapsulant Films

As reported in Section 2.2, information on the chemical structure of the polymer resin was only provided for around 10% of the encapsulation films examined. However, many relevant encapsulant film properties are not solely dependent on the resin alone, but also on the additives, see Figure 11. In addition to polymer resin, typical PV encapsulation films also include

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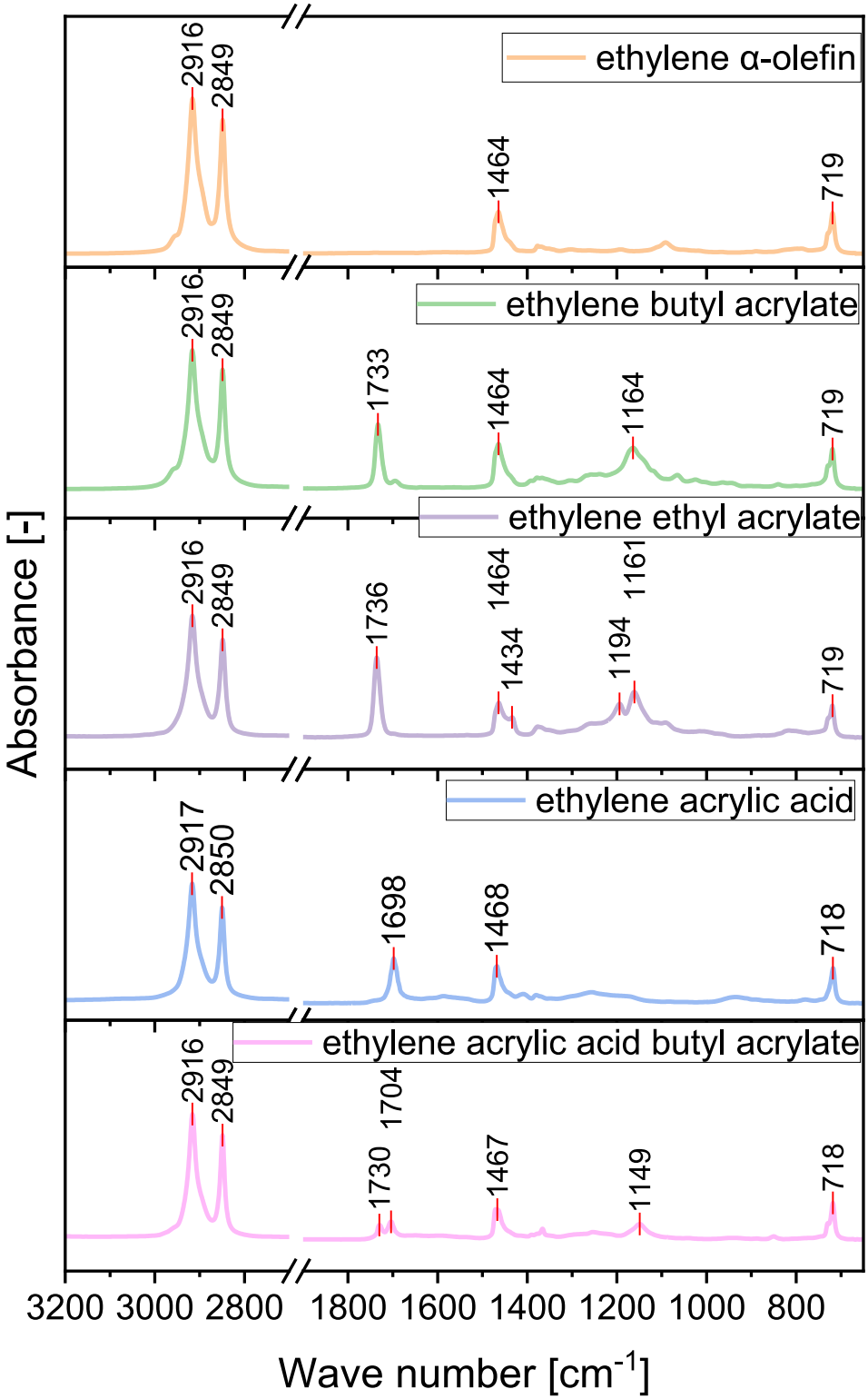

FIGURE 9 | FTIR ATR spectra, representing the five polymer chemical structures of the monolayer encapsulants analyzed in Table 3 in the supplement.

crosslinking agents (with the exception of thermoplastic encapsulants), adhesion promoters, UV absorbers, and various primary and secondary antioxidants, as outlined in Table 2. Selecting the right stabilizers is essential for ensuring the long-term stability of encapsulants and, by extension, minimizing the degradation of PV modules over their lifespan. However, it is worth noting that additives themselves can contribute to or even initiate degradation processes in PV modules [4, 6, 150].

Figure 11 depicts key properties of encapsulant films relevant to module production, efficiency, reliability, and electrical safety. Only a handful of the literature papers identify

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complete recipes for the encapsulant films, including type and quantities of curing and adhesion additives as well as stabilizers [4, 88, 113, 148, 156–158].

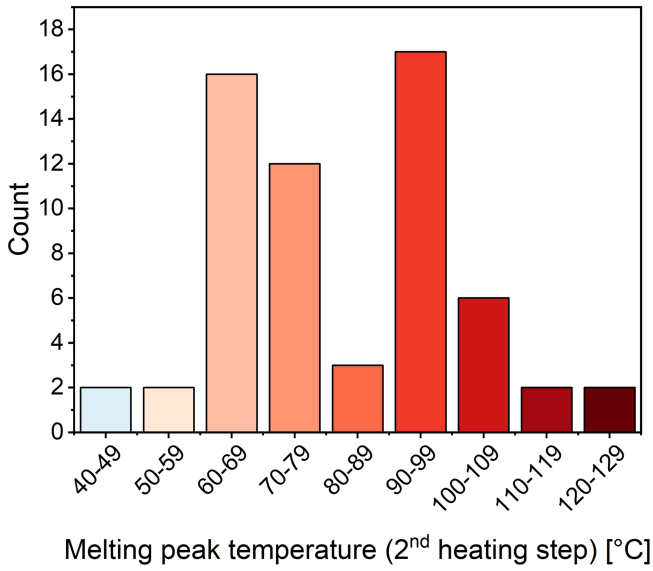

FIGURE 10 | Melting temperatures of the collected encapsulants calculated on the second heating step of DSC measurements.

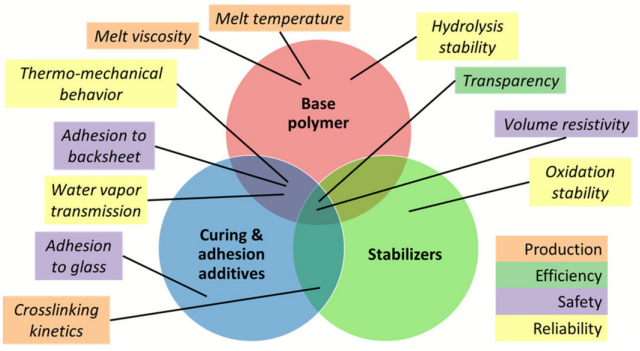

FIGURE 11 | The dependence between resin, cure, and formulation is identified relative to encapsulant properties, important to the production, efficiency, safety, and reliability of PV modules.

The chemical structure as well as the molar mass distribution of the base polymer is most relevant to module lamination, as it defines melting temperature and melt viscosity [159]. Also, the sensitivity of a polymer to hydrolysis—degradation due to reaction with water vapor—largely depends on its chemical structure. Specifically, the presence or absence of certain chemical bonds within the polymer determines its propensity to hydrolytic degradation [160]. Polymers like EVA contain ester bonds in their chemical structure. These bonds are susceptible to hydrolysis, meaning that when EVA is exposed to moisture over time, these bonds can break, leading to hydrolytic chain scission [160, 161]. In contrast, ethylene/α-olefin copolymers do not contain ester bonds. Their chemical structure consists entirely of hydrocarbon chains, which are much less reactive with water molecules [48]. By comparison, the oxidation stability of encapsulation films based on ethylene copolymers is enhanced due to the stabilization system, which usually consists of UV absorbers, primary and secondary antioxidants (radical scavengers, hydroperoxide decomposers) [4, 6, 160]. As polyethylene and ethylene copolymers are not intrinsically stable towards oxidation, without proper stabilization they degrade within several hundred hours of direct xenon exposure [43].

Cure and adhesion additives include silane coupling agents, peroxide crosslinkers, and crosslinking coagents, which serve to accelerate network formation during crosslinking [4, 6, 162]. Prior to lamination, all encapsulation films are thermoplastic materials. By crosslinking the polymer chains during module lamination, a flexible and transparent encapsulation layer is created. This process involves forming a 3D polymer network, which significantly enhances the material's mechanical and thermal stability. The amount as well as the type of crosslinking agent used can also influence the thermo-mechanical properties of the encapsulant. Different crosslinking agents can lead to variations in the degree of crosslinking, the network structure, and the resulting properties [9, 11]. Also the processing conditions, such as temperature and time, can affect the crosslinking reaction and the resulting properties of the encapsulant [148]. By constraining a polymer chain's ability to rearrange, crosslinking typically reduces the degree

TABLE 2 | Typical curing and adhesion additives and stabilizers used in encapsulants based on ethylene copolymers (96–98 wt.%) [4, 6, 7, 156–158].

	Function	Type	Weight%	Common examples
Curing and adhesion additives	Base polymer	Ethylene copolymers	96%–98%	EVA, polyolefins
	Curing agent	Peroxides	1–2	Luperox TBEC, Luperox
	Curing co-agent (initiators)	Triallylisocyanurate, triallylcyanurate	N.A.	Taicros
	Adhesion promoter	Trialkoxy silanes	0.2–1	Silane A 174, Dynasylan
Stabilizers	UV absorber	Benzophenones, benzoltriazoles	0.2–0.35	Tinuvin 234, Cyasorb 531, Chimasorb 81
	Primary antioxidant	Hindered amine light stabilizers (HALS)	0.1–0.2	Tinuvin 123, Tinuvin 770
	Primary antioxidant	Sterically hindered phenols	N.A.	BHT
	Secondary antioxidant	Phenolic phosphonites	0–0.2	Irgafos 168, Naugard P

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TABLE 3 | Summary of key properties for ethylene-based encapsulants [142], based on information from the literature and manufacturers' data sheets. Within a given material class, these parameters can vary significantly depending on the specific polymer formulation but also testing conditions.

Encapsulant (thickness 0.45–0.5 mm)	WVTR [g/m²/day]	Water absorption [%]	Volume resistivity at 23°C [Ω·cm]
EVA	15–25	0.2–0.3	10^{13}–10^{14}
POE (peroxide crosslinked)	≤5	<0.1	10^{14}–10^{17}
TPO (thermoplastic)	≤1	<0.1	10^{15}
Ionomer	≤1	<0.1	10^{16}

of crystallinity relative to that of the base polymers in the encapsulant films, resulting in a reduced mechanical modulus below the melting point [9, 11, 147].

The crosslinking kinetics are mostly defined by the peroxide crosslinker(s) and crosslinking accelerator(s) [11, 162]. Peroxide crosslinkers decompose upon heating to generate free radicals. These free radicals initiate the crosslinking process. This reaction turns the polymer into a more stable and durable network [9]. The kinetics of this crosslinking process—how quickly and completely it occurs—are heavily influenced by the type of peroxide used, its concentration, and the temperature at which the reaction takes place [163]. Different peroxides decompose at different temperatures and rates, thus affecting the overall crosslinking kinetics [9, 11, 65, 164]. Crosslinking accelerators are additives that enhance the efficiency of the crosslinking process [11, 165, 166]. The most common substance (by far) in this category is triallylisocyanurate, whose principal effect in accelerating crosslinking is understood to be its multifunctional bonding, allowing for more rapid creation of a network [167]. But not just the curing adhesives influence the crosslinking kinetics of the material. A recent publication found that radical scavengers that are used for stabilization can interfere with the radical formation in the crosslinking process, slowing down the curing process [148].

In comparison, ionomers undergo a physical crosslinking process, where the ionic groups cluster together due to electrostatic attraction [22]. These ion clusters act as physical crosslinks, holding the polymer chains together. The strength of these physical crosslinks depends on several factors such as ion concentration, ion type and the polymer matrix. The formation of physical crosslinks has a significant impact on the properties, such as increased tensile strength, modulus, and toughness. Physical crosslinking can also increase the thermal stability of ionomers, raising their glass transition temperature and melting point. Ionomers often also exhibit improved resistance to solvents and chemicals due to the reduced chain mobility caused by physical crosslinking [168–170].

Adhesion of the encapsulant film to the front glass and the solar cell is primarily defined by the coupling agent [105, 162]. However, the adhesion of the encapsulant to the polymeric backsheet is also influenced by the chemical composition of the encapsulant base polymer. For example, polyvinyl fluoride (PVF) is a polymer known for its durability, chemical resistance, and excellent weatherability, making it a popular material in PV module backsheets. However, one of the challenges with PVF is its relatively low surface energy, where it does not naturally bond well with other materials. In order to achieve good adhesion to encapsulant films, the PVF surface is typically equipped with a primer [171]. Another example would be the combination of ethylene-based encapsulants and PP-based backsheets. Although both HDPE and PP are POs and composed solely of hydrocarbon groups, they are immiscible polymers. This means that when mixed or brought into contact, they do not blend or adhere to each other effectively [48, 172]. However, the compatibility of ethylene/α-olefin copolymers and PP is highly dependent on the used α-olefin type and content.

The WVTR of the encapsulant film depends on the chemical structure and the morphology, i.e., the crystalline structure and polymer chain orientations of the base polymer as well as the degree of curing. The rate and efficiency of permeation are influenced by the materials properties, the nature of the permeant, and environmental conditions like temperature and humidity [27, 75, 102, 173–175]. While the chemical structure of the base polymer defines the absorption as well as the diffusion process of water vapor, an increase in the degree of curing reduces the chain mobility, also reducing the diffusion rates of small molecules like water [176].

Transparency of the encapsulant film is dependent on all components. The base polymer and its crystallinity usually define the transparency of the material [44]. However, an increasing degree of crosslinking also increases the transparency via a reduction of the scattering losses due to reduced crystallinity [59, 177, 178]. The use of UV absorbers on the other hand decreases the transparency in the ultraviolet range of wavelengths.

The volume resistivity of the encapsulant is dependent on all components. Polymers in general are electrically insulating [159]. However, the chemical structure of the polymer defines the water uptake, which may influence ion mobility. Usually, polar EVA films have a volume resistivity one or two orders of magnitude less than non-polar ethylene/α-olefin based polymers [179]. Also the stabilizers were found to have an influence on volume resistivity [180]. Table 3 provides a summary of key properties of ethylene based encapsulant films.

There is a general trend that stabilizers tend to migrate and segregate on the surface more readily in non-polar polymers compared with polar polymers [181]. However, the specific interactions between the stabilizer and the polymer, as well as the factors of resin, degree of crosslinking, and additives can significantly impact the actual migration behavior. This could potentially impact the shelf life of encapsulant films as well as the reproducibility in manufacturing [114, 182]. It is important to note that the polarity of a polymer is not the only factor influencing stabilizer migration. Other properties like molecular weight and crosslinking also play a role.

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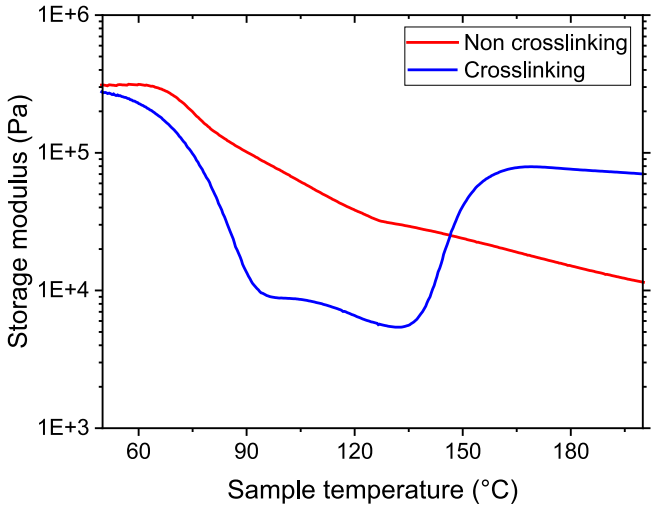

FIGURE 12 | DMA measurement of crosslinking ethylene α-olefin copolymer (blue) and a non-crosslinking latent cure VTMS grafted ethylene copolymer (red), with no prior lamination or aging history.

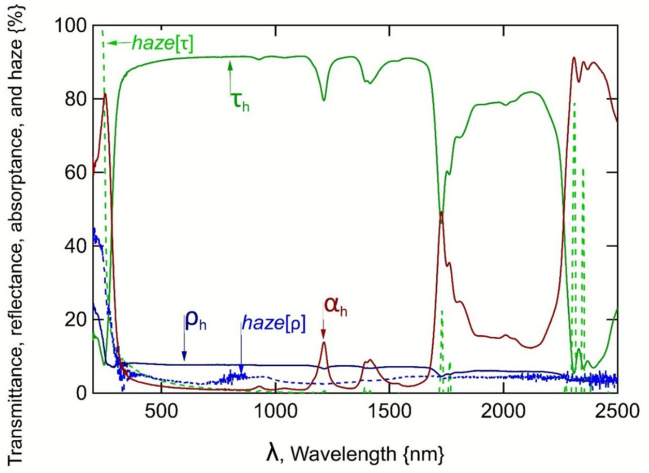

FIGURE 13 | Optical performance of the UV-transmitting TPO-5 from [72], including the hemispherical transmittance (τ_h), hemispherical reflectance (ρ_h), and hemispherical absorptance (α_h)—all obtained using an integrating sphere—as well as the haze (quantifying the optical scattering, based on the difference between τ_h and τ_d or the difference between ρ_h and ρ_d), where the direct transmittance (τ_d) and direct reflectance (ρ_d) were obtained without an integrating sphere.

4 | Performance of Ethylene Copolymer Based Encapsulants

4.1 | Influence of Encapsulant Properties on Module Lamination

Chemical structure and formulation (including additives) influence the thermal behavior of the polymers during lamination [148]. Thus, it is necessary to determine the temperature ranges where significant transitions take place for each material. The two main transitions that can take place during processing are: (I) the melting of the crystalline phase and (II) crosslinking (for encapsulants formulated with a free-radical generator). Ethylene copolymers are semi-crystalline, which means that the crystalline content can melt decreasing the viscosity and allowing the polymer to flow between or soften and adhere to the other materials constituting the PV module. It is necessary to know at which temperature the crystals begin to melt to determine the minimum temperature that should be reached during lamination. Additionally, if the encapsulants chemically crosslink during lamination, it is desired to know the relationship between temperature and crosslinking reaction kinetics in order to allow the reaction to proceed until the desired crosslinking degree is reached.

Thermomechanical properties and viscoelastic behavior can be assessed with dynamic mechanical analysis (DMA). The results of DMA measurements performed on two encapsulants (crosslinking and non-crosslinking during lamination) are shown in Figure 12. It is possible to see that, for the crosslinking material, the storage modulus decreases between 50°C and 90°C, followed by a further decrease between 90°C, and again at 135°C. At this temperature, the modulus begins to increase until it reaches a plateau at about 165°C. The decrease of the modulus corresponds to the melting phase of the crystalline structures; the increase, instead, corresponds to the occurrence of the crosslinking reaction. The sample that does not chemically crosslink during lamination shows a decrease in the storage modulus until about 120°C and a further decrease, but with a lower slope up to 200°C. At 135°C, there is almost one order of magnitude of difference between the storage modulus values of the two materials, indicating that the non-crosslinking sample does have a higher viscosity than the crosslinking sample [48].

4.2 | Influence on Module Performance

The performance of contemporary encapsulants in a PV module may be affected by the resin, the choice of additives, and the subsequent manufacturing processes. As represented in Figure 13, POs may be more prone to optical scattering; see Equation (1):

$$haze\,[\tau] = \frac{(\tau_h - \tau_d)}{\tau_h} \tag{1}$$

The equation represents the ratio of the scattered to the total transmitted light. The hemispherical transmittance, τ_h (%), or reflectance, ρ_h (%), is obtained using an integrating sphere (ideally, an angle of acceptance of ±180°, but in practice probably more similar to the angle of acceptance of a PV module ~±60° [183]. No integrating sphere was used to measure the direct transmittance, τ_d (%), or direct reflectance, ρ_d (%), which is estimated to have an angle of acceptance of ±2°–3°. The hemispherical absorptance, α_h (%), is determined from the sum: $100 = \alpha_h + \rho_h + \tau_h$. In the figure, τ_h typically exceeds 90% from 1250 nm down to 255 nm. ρ_h instead is steady at ~7.5% from 1250 nm down to 350 nm. ρ_h for a PV module would be half of the glass/encapsulant/glass coupon (which has 2 glass/air interfaces) in Figure 13. α_h is ~1.9% from 1250 nm down to 300 nm, consistent with the good optical throughput of an unaged, representative PO encapsulant [184]. The average haze in transmittance of 3.5% occurs from 300 to 830 nm. The average haze in reflectance of 3.8% occurs from 300 to 830 nm.

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Figure 13 clarifies that most scattering occurs at UV–Vis wavelengths, where some but not all photons may be recovered by internal reflection once the incident light has entered the PV cell. Haze may be visually observed as gray in color, where the image quality is reduced when looking through the encapsulant. In EVA, the VA side-groups limit crystallization, more so in the older 33% VA content (VAc) resins historically used to limit loss of optical transmittance, than in the 28% VAc materials which are commonly used nowadays. Peroxide induced crosslinking also limits crystallization. The crystalline content in any of the ethylene-based encapsulants is metastable, where its concentration and predominant structure(s) will evolve with aging or quenching from the melt state [43, 145]. For latent curing encapsulants, the curing takes place at room temperature after formation of the polymer crystallites. Contemporary encapsulants may be formulated to be UV-transmitting or UV-blocking formulations, e.g., where the use of UV absorbers and UV stabilizer additives give a UV cut-off wavelength (becoming 10% transmitting) from 255 to 360 nm, respectively.

The crystalline content may decrease with aging, resulting in an increase in transmittance with corresponding decreases in haze and the yellowness index with weathering [72, 138, 185]. Early improvements in optical performance may, however, be followed by reduced transmittance in the event of decomposition and subsequent formation of chromophores from the additives or polymer [186].

4.3 | Influence on Common Degradation Modes

As previously mentioned, thin film PV technologies—which presently constitute only a very limited share of the global PV market (< 3%)—were highly sensitive to moisture. For this reason, thin film PV modules were often adopting a glass/glass structure, with the rear and front glass covers providing an excellent barrier to water. However, extensive research was dedicated in the first decade of the century to replace high WVTR EVA with other encapsulants. As an example, an encapsulant often used in the manufacturing of CIGS solar panels was low WVTR ionomer [27, 36].

Conventional wafer-based crystalline silicon solar cells—such as aluminum back surface field (Al-BSF) and later passivated rear emitter (PERC) cells—are not known to be particularly affected by moisture-induced degradation. These solar cells are in fact frequently used in modules with a glass/foil structure (a structure partly permeable to water) and adopting EVA as an encapsulant. Moisture ingress can in the long run cause some oxidation of the metallic contacts. In reality, as mentioned earlier, what is more critical for the corrosion of metallic interconnects is the generation of acetic acid in EVA, which can be accelerated by the presence of humidity in the laminate [187, 188].

Presently, the global solar market is rapidly transitioning to high-efficiency solar cells based on n-type silicon wafers. Mainly, two solar cell architectures exist: (a) SHJ and (b) TOPCon, with the latter seemingly becoming the dominant platform, at least in the next couple of years [14].

Both technologies exhibit a pronounced sensitivity to moisture and water. In the case of **SHJ solar cells**, the high sensitivity to water has been fully understood only recently [62, 112] and is reinforced by the adoption of glass as a front or rear cover. The adoption of encapsulants with a relatively high water uptake (such as EVA), favors a corrosion reaction of the glass cover(s) releasing sodium (Na) ions that, in combination with water, form molecular sodium hydroxide (NaOH). This can percolate through the encapsulant and the transparent conductive oxide (TCO), eventually reaching the solar cell. Na ions may act as recombination centers in the passivating layers or at the a-Si/c-Si interface, reducing the cell's passivation properties. Therefore, it is more correct to talk of a combined sensitivity to water and glass, which in SHJ modules can be mitigated or suppressed at the module level by using a high-volume resistivity encapsulant with a low WVTR—such as POs—or by encapsulating SHJ solar cells in a configuration impermeable to water.

Topcon solar cells are a more recent technology, with a more limited knowledge in terms of reliability. Their considerable sensitivity to moisture is often explained by the adoption of Al/Ag metal pastes used to print the front interconnects [96, 119]. The industry seems to have recently understood the root cause of this sensitivity to moisture and optimized the firing process to adopt metal pastes with a very low or no content of Al, making these solar cells less prone to moisture-induced degradation mechanisms [189]. For this reason, the adoption of PO encapsulants is generally suggested as an encapsulant choice for Topcon cells. In reality, as argued by Sen et al. [119], the compatibility of Topcon with PO encapsulants coming from different suppliers (and with different formulations) should be thoroughly checked, as problems with the wrong choice of additives may arise.

4.3.1 | Delamination

Generally, delamination can be caused by environmental stresses and external mechanical loads due to wind or snow. Depending on the material and process parameters, the interfaces of the encapsulant to glass, cell or backsheet can delaminate. The critical thresholds for delamination were determined to be in the range of ~160 J/m^2 for cell/encapsulant and ~10 J/m^2 for backsheet/encapsulant [190]. Glass–glass modules may contain higher interfacial stresses compared with glass–backsheet modules [70], facilitating delamination. Delamination was frequently observed in early glass–glass modules due to degradation-induced changes in interfacial chemistry between EVA encapsulant and glass [70]. The degradation of EVA was thereby typically accelerated by acetic acid formation, which has been found to catalyze the hydrolysis of siloxane adhesion promoters [191]. Because PO encapsulants do not produce acetic acid, improved robustness is expected as observed in [192].

A comparison of the peel strength of encapsulants to both cell and glass in PV modules with ethylene α-olefin copolymer or EVA showed stronger initial adhesion in the samples with PO, but similar values for both EVA and PO after damp-heat aging [70]. However, due to the lack of experience with PO encapsulants and the large variety of process parameters, it can require more effort to determine the optimal lamination parameters. Compared with EVA, which is a well-known material

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with similar properties (across different manufacturers), this increases the probability of improper lamination, and therefore also for issues like delamination (compare Section 5.1 Manufacturing).

During the module lifetime, polymer aging and possibly post-lamination curing influence the mechanical- and adhesion properties. These factors can contribute to triggering delamination, but also might hinder the appearance of the phenomenon of delamination. Similar behavior has been observed in a humidity–freeze test [193] of PV modules that had previously developed signs of delamination in the field (Figure 14).

Despite the good initial adhesion of PO encapsulants to other module components, long-term studies on the development of mechanical properties and adhesion are lacking. Considering the variation of composition of PV encapsulation products, this leaves a relatively high risk of unexpected behavior and reliability issues. One of the possible future issues could be the loss of adhesion to the backsheet, as there currently exists a large variety of backsheet products with different layer stacks, and it is often not known if the inner layer is specifically optimized for adhesion to EVA or a specific PO [138, 185].

4.3.2 | Potential Induced Degradation (PID)

PID encompasses a variety of degradation mechanisms that can occur in PV cells, including shunting, polarization, corrosion, and delamination, which are triggered by the high potential differences that may arise between grounded frames and polarized solar cells [90, 118, 182, 194]. PID by shunting (PID-s) is associated with sodium ion (Na^+) transport from glass to the solar cell. Thus, the encapsulant can be a barrier for sodium ion transport to mitigate this degradation mode. It has been demonstrated that POE-based encapsulants reduce susceptibility to PID-s due to impermeability of POEs to Na^+ ions [179, 182]. Whereas EVA with higher volume resistivities is less prone to PID [195], this parameter is not the determining factor for susceptibility to PID-s of POEs, as POEs with volume resistivity ranging over several orders of magnitude demonstrated similar performance. Meanwhile the susceptibility of a module to power loss can be associated with non-specific charge transport through the encapsulant, such that the total conductivity of the encapsulant is a critical property for determining performance [113]. The volume resistivity of different POE resins can vary over several orders of magnitude (i.e., from about 10^{14} to 10^{17} Ohm-cm, whereas EVA resins typically have volume resistivity in the range of 10^{13} to 10^{15} Ohm-cm). PID-p can be mitigated with the use of encapsulants with high volume resistivity, but performance is also dependent on other formulation components in the encapsulant film and on the particular test conditions used, such as illumination conditions.

4.3.3 | Corrosion

In the presence of moisture and heat, hydrolysis reactions will occur generating acetic acid [187]. With the addition of UV radiation, photodegradation initiates faster from vulnerable VA groups, followed by the decomposition of the main chain by

FIGURE 14 | Detailed photographs of a PV module with delamination between encapsulant and backsheet at the module edge; after field-ageing (top) and subsequent accelerated aging (humidity–freeze, bottom).

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Norrish type chemical reactions [196]. EVA formulations have improved considerably over the last decades with the introduction of additives to delay this process, e.g., UV blockers, antioxidants, and acid scavengers [150, 156, 157].

In the long run, degradation of EVA leads to the generation of acetic acid, along with discoloration, and possibly corrosion of the cell's anti-reflective coating. Acetic acid can also attack the cell's metallization (fingers, busbars, and ribbons), leading to an increased series resistance and consequently a reduced fill factor (FF) and decrease in performance [4, 112, 197].

Further, in glass/backsheet modules, the permeability of the polymeric foil allows slow release of the acetic acid into the environment [134, 198]. This does not happen in glass/glass structures, for which acetic acid remains trapped in the less permeable structure of the module. The acid generation process in EVA is self-catalytic making its impact for glass/glass modules significantly riskier. For this reason, the broad adoption of bifacial glass/glass modules in recent years has been one main driver for the adoption of PO encapsulants from the market.

The absence of VA groups in POs avoids the generation of acetic acid and related degradation phenomena. In PV encapsulants, however, besides the base resin, other additives and environmental stressors can produce acidic species, leading to the corrosion of the cells and metallization in the modules. Therefore, the presence of acidic ingredients in POs including additives and their corresponding degradation cannot be a priori completely ruled out, but due to the very low initial concentration of additives in general [4, 6, 7], the impact on module reliability over the modules' operational lifetime (30 years and beyond) is expected to be lower for POs than for EVA, where significantly higher concentration of acid can be generated from the base resin itself [4, 187].

5 | Discussion: How Do PO-Based Encapsulants Compare to EVA in Terms of Long-Term Durability, Processing Efficiency, and Overall Performance in PV Modules?

The development of a quasi-standardized formulation for EVA was a process that spanned over a decade, primarily throughout the 1980s and part of the 1990s. During this period, various field-related issues arose, such as the well-documented yellowing and corrosion observed in PV modules at Carrizo Plains, California, USA [4, 150, 199]. The worst reported case of degradation in this region was attributed to slow-curing EVA, exacerbated by the low-concentration system at the site (i.e., meaning that the modules were exposed to higher levels of irradiance). This field incident highlights the challenges faced by early EVA formulations. For instance, the so-called standard-cure EVA formulation, A9918, was prone to discoloration [150, 197]. The discoloration has been linked to interactions between crosslinking peroxides and certain stabilizing additives, as well as possible oxidation of the encapsulant. However, no evidence of conjugated double bonds, suggested as a cause of discoloration in earlier studies, was found in the discolored, field-aged EVA encapsulant [150, 186]. This discoloration and other degradation phenomena, such as corrosion, were linked to chemical interactions within the encapsulant, as well as environmental factors including exposure to UV light and oxygen [4]. In response to these issues and in the advent of newer peroxides and UV absorber additives, EVA formulations were gradually improved. By the early 1990s, efforts to reformulate EVA to mitigate discoloration and enhance durability in the field had yielded better results [4, 150]. Encapsulant film and module manufacturers have therefore spent more than 30 years on optimizing (and standardizing) EVA films and processes, and still additional changes in the EVA formulation have been introduced in recent years to tackle the module degradation related to ion migration, snail trails, acid generation, and PID [180].

The adoption of POs (particularly POE) started in the early 2010s [131], but a substantial uptake started around 2017–2018 [14, 15]. From a market perspective, the adoption of PO-based encapsulants has been significantly influenced by the industry's shift towards bifacial cells and modules, along with the increased use of double-glass structures. This transition has driven substantial growth in the use of POs, particularly in the larger utility-scale installations. The bifacial modules, designed to capture light from both sides of the panel, benefit from the enhanced durability and optical properties of PO encapsulants, especially when combined with double-glass configurations.

In contrast, other applications of PO encapsulants, such as in lightweight [200, 201] or vehicle-integrated photovoltaics (VIPV) [124], remain at an early stage of development.

As discussed earlier, we are still far from having standardized PO formulations. As a result, new formulations are constantly being developed tailored to the emerging cell structures and interconnection technologies [138]. Understandably, this situation raises concerns in production and about the potential long-term performance and reliability of the PV modules manufactured with PO encapsulants, particularly considering possible compromises in material performance due to the pressure of cost reduction in recent years.

5.1 | Manufacturing

Some of the PO's advantages originate from their non-polar or less polar nature leading to a much higher volume resistivity, lower WVTR, and reduced ion transport compared with EVA. On the other hand, their non- or less-polar nature results in lower solubility of most additives (which are generally more polar) in the polymer matrix. Additives in POs therefore tend to migrate to the surface and either create a kind of surface layer (e.g., in the form of a powder) or are outgassed from the film. The migration and release of additives from the film create multiple challenges in module manufacturing:

I. **Storage time and conditions** (and consequently shelf life) of the encapsulant rolls before lamination—already important for EVA, particularly for glass/glass structures [112]—become critical parameters to respect.

II. **Lamination processing** windows and parameter need to be strictly fine-tuned to each encapsulant. The formulation of the POE encapsulant may differ greatly across

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different suppliers and different grades in terms of the base resin selection and additives package selection as compared with EVA encapsulant, which lead to a wider range of curing kinetics during the module lamination process. As a result, typical EVA encapsulants tend to exhibit wider processing windows and are, therefore, more "forgiving" in terms of process deviations [65].

III. To **speed up the manufacturing processes** (and reduce running costs), certain PO grades are formulated to exhibit faster curing rates at lower lamination temperatures. In the post-lamination quality control, the criteria over the gel content of POE differs among grades, ranging from typically 60% to 80% [89]. As a comparison, thanks to its more standardized curing solutions, the gel content criteria of EVA is widely accepted to be between 80% and 90% [9, 149].

As a result of the previous three points, for POs, it is more important to optimize the lamination cycle for each specific grade in order to obtain qualified module lamination quality, including an optimal and uniform **curing and adhesion** to glass or a backsheet, increasing, therefore, reproducibility challenges and potentially impacting manufacturing line efficiencies.

5.2 | Field Reliability

With respect to solar PV modules, ultimately what matters is field reliability and long-term performance, as these will impact the profitability of solar projects in addition to the LCOE (levelized cost of electricity) and carbon intensity of the generated solar electricity [202, 203]. Expected service lifetimes of solar panels (reflected by industry standard performance warranties) have recently increased from 25 to 30 or even 35 years.

A significant track record of 40+ years exists for fielded solar PV modules manufactured with EVA, which is not the case for modules manufactured with POs, as nearly no history is available (time series are presently limited to 5–10 years). In addition, system developers (also module and encapsulant manufacturers) may not be eager to share data or findings, so that data available in the literature is extremely limited.

As mentioned in the previous section, some of the manufacturing challenges related to the adoption of POs (i.e., the difficulty in obtaining an optimal curing and adhesion of the different sandwich layers and process variability), are exactly what could endanger the reliability and durability of PO encapsulated modules if not properly optimized and controlled.

POs may provide a reliability advantage relative to EVA (due to their lower ion migration, water uptake, and acid generation), but these advantages may not be realized in the long run if there are failure modes, such as delamination, that arise from inappropriate formulations and suboptimal processing. Delamination, which leads to water ingress in the modules, may propagate over time and can not only trigger several other degradation modes, but can also lead to insulation losses [204] and the generation of hot-spots, thereby impacting the operational safety of solar panels and strings. More reporting of field reliability data for different encapsulants will help build a track record of reliability performance that can aid in future material selection decisions.

5.3 | EPE Coextruded Films

POs remain more expensive than EVA (1.5–2 $/m^2 vs. ~1 $/m^2 for EVAs). Besides the higher costs, some of the limitations of POs discussed in this section might have slowed down the adoption of POs in the market (see Figure 1, for encapsulant market share). In fact, a recent solution adopted by module manufacturers is the use of EVA/POE/EVA (EPE) coextruded encapsulant films, where a POE layer (typically 200–300 μm) is sandwiched between two layers of EVA. EPE has already gained a market share of around 10% in 2023 [15]. Besides being less costly than monolithic POE encapsulants, these coextruded films may overcome some of the limitations of POE encapsulants (notably the poor adhesion and slower processability during the lamination) as the adhesion to the cell or glass substrate is provided by the EVA layers. EPE, however, simultaneously retains the advantages of POE films including lower WVTR and higher volume resistivity.

The adoption of EPE films might come with some advantages in productivity, but the presence of EVA in the material means it still allows the shortcomings of the EVA encapsulant, such as the potential acetic acid generation inside the module. In addition to the shortcomings of EVA, the performance and durability of the EVA and POE interfaces (materials of intrinsically different polarity) pose a new risk. Furthermore, migration of additives between the different layers could result in changes in lamination performance or final mechanical properties depending on the age of the encapsulant film. Separately, the interfaces between EVA and POE may allow more rapid mass transport (water or oxygen), facilitating corrosion processes within a PV module. If the track record of field-deployed PV modules containing POs is limited, this is even more true for modules with EPE encapsulants. Therefore, the potential and reliability of EPE-containing modules still need to be demonstrated in the field. However, EPE encapsulants were not part of this investigation and therefore are not listed in Table 1.

5.4 | Comparability of Published Results

This review demonstrates that encapsulant films marketed as PO, POE, or TPO showcase a variety of chemical structures, curing chemistries, and a broad range of melting temperatures (see Table 1). The wide variety of materials with different properties indicates that the commonly used designation "polyolefin" is frequently used improperly, and additionally is descriptive of a much broader class of materials than relatively specific terms like EVA with which it is frequently juxtaposed.

Moreover, in scientific literature the terms POE and TPO are in most cases used as synonyms for one material instead of for a class of materials. Typical studies that have been reviewed for this paper consist of a work plan that, in order to test a hypothesis, varies the encapsulant film (EVA vs. POE vs. TPO). In most cases, the chemical structure of the base polymer of the encapsulant film is not given, and the topic of the influence of additives and stabilizers on the investigated property is rarely

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discussed. Problematically enough, many studies come to conclusions like "POE performs better than EVA" or "TPO helps to mitigate a certain failure mode," assuming all materials that are marketed as POE or TPO behave sufficiently similarly. The same issue applies for published work on lamination and process optimization. In reality, however, without the information on the chemical structure of the base polymer and the complete additive composition of the encapsulant, along with lamination conditions, results may lead to totally inaccurate conclusions.

To make research results comparable, a better categorization and classification of encapsulant films is necessary. A method to categorize common commercial PV encapsulation materials is highlighted in the matrix in Figure 15. By far, the greatest volume of PV encapsulants is the peroxide-cured EVA and peroxide-cured POE materials. Note that encapsulants that have been referred to as "TPO" encapsulants are often VTMS-g-POE or ethylene/acrylate/VTMS terpolymers that, while thermoplastic during lamination, can cure later in the presence of moisture via condensation of the alkoxysilane functionality [98]. Additionally, melting temperature and optical characteristics should be given. In the best circumstances, also the additive composition is given. However, this information is typically proprietary to either the raw material suppliers or the encapsulant manufacturers, and therefore is seldom publicly available.

One major challenge in understanding the reliability of encapsulants is the lack of studies that investigate the role of stabilizers and additives in encapsulants and their contribution to the degradation modes in PV modules. It is important to encourage the consistent documentation of manufacturers and the detailed chemical composition including the additives in research studies.

6 | Summary and Conclusions

Up to November 2024, 228 indexed publications have addressed so-called PO encapsulants, with 391 encapsulant films investigated. Among these, only 15.8% list their manufacturer, and just 11.5% provide detailed information on the base polymer's chemical composition. In the early years ionomers and unspecified POs were the most investigated materials, while after 2020 the focus shifted to "POE" and "TPO" encapsulants.

The market inventory in this study, as of October 2024, includes 74 different encapsulant types from at least 26 different manufacturers, focusing on verified materials characterized by the co-authors' institutions. These materials utilize five base polymers, two curing chemistries, and also include non-curing thermoplastic encapsulants—with variations in properties such as softening onset, shear viscosity, and optical properties. The melting temperatures of the investigated encapsulants range from 49°C to 121°C, with production dates spanning from 2006 to 2024. Only a few publications investigated the role of additives and stabilizers in encapsulants, even though they are responsible for many essential encapsulant film properties related to the production, efficiency, safety and long-term reliability of PV modules.

Ethylene-vinyl acetate copolymers (EVA) have a 40+-year track record in solar PV modules, whereas POs lack long-term field data, with available history limited to 5–10 years. Furthermore, the PV industry is hesitant to share findings making field data harder to aggregate. Challenges with POs include achieving optimal curing, adhesion, and managing process variability, which could compromise reliability and durability if not properly controlled. While POs offer advantages like a lower ion migration rate, reduced water uptake, and minimal acid generation, they may be more prone to delamination due to chemical polarity, formulation and process issues.

The successful EVA encapsulant optimization over the last 40 years is not directly transferable to new PO-based encapsulants. It is important to note that the path to a more standardized formulation of EVA was complex and iterative, reflecting the evolving understanding of material science in the context of PV technologies. As EVA became more reliable, challenges

			Lamination or crosslinking		
			Cured	Non-cured	
				Latent Cure	Thermoplastic
Resin	Ethylene Polymers	Polyolefin	• Peroxide cured POE		
		Ethylene/polar copolymers and terpolymers	• Peroxide cured EVA	• Ethylene/acrylate/VTMS terpolymer	
		Grafted or Post-reactor modified polymers		• VTMS-g-POE	• Ionomer (Ethylene/acrylic acid copolymer) • MAH-g-POE • Ethylene/acrylate/GMA terpolymer
	Other Polymers		• Silicone, e.g., "PDMS"		• PVB • TPU

FIGURE 15 | Categorization of some common encapsulants using a two-dimensional taxonomy. GMA, glycidyl methacrylate; MAH-g-POE, maleic anhydride grafted POE; PDMS, polydimethylsiloxane; PVB, polyvinyl butyral; TPU, thermoplastic urethane; VTMS, vinyltrimethoxysilane.

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still persisted, and even today, new issues and material innovations continue to arise. The shift towards PO encapsulants presents even greater complexity when considering the broad range of different polymers that have been lumped together under the umbrella of PO. Unlike EVA, which has been narrowed down to a relatively well-defined material formulation, PO represents a broad class of materials, each with different properties and performance characteristics. Achieving standardized formulations for PO encapsulants requires a more accurate classification of the different base resins being used.

This study emphasizes the need for more precise terminology. Scientific literature often generalizes findings about these materials, despite the lack of information on base polymer composition, additives, and stabilizers—which are rarely discussed. As a result, many conclusions comparing encapsulants may be misleading due to the variety of material formulations. Therefore, a comprehensive categorization of encapsulant films is proposed, considering factors including curing mechanisms, melting temperatures, and optical properties. The authors invite and ask the PV community to use the categorization scheme and—if necessary—further develop it to support the development and optimization of encapsulation materials' properties and reliability.

Each class of ethylene copolymer encapsulant provides advantages and disadvantages relative to EVA encapsulants. Proper classification and description of these different encapsulation materials will help build a library of data on lab and field performance that can be used to better understand the long-term reliability of these newer encapsulation materials.

Author Contributions

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data supporting this article have been included as part of the Supporting Information.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Table S1:** Statistical evaluation of literature investigating polyethylene copolymer based encapsulants. **Table S2:** List of publications investigating polyethylene copolymer based encapsulants (as of November 2024).

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