

A Polyolefin Elastomer Encapsulant Modified by an Ethylene–Propylene–Diene Terpolymer for Photovoltaic Applications

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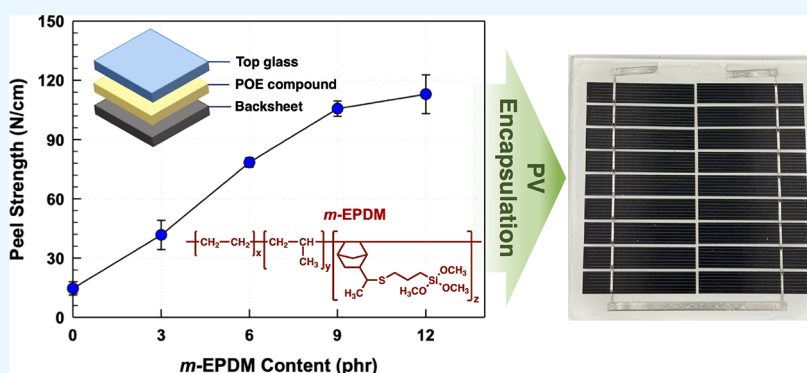


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ABSTRACT: In this study, a newly designed adhesion promoter, a modified ethylene–propylene–diene terpolymer (*m*-EPDM), was constructed *via* a simple thiol–ene click reaction between the ethylene–propylene–diene terpolymer (EPDM) and 3-mercaptopropyltrimethoxysilane (MPTS) to employ polyolefin elastomer (POE) encapsulants in photovoltaic modules. The grafting reaction of MPTS on an EPDM backbone (thiol–ene click reaction) was verified using ^1H NMR, ^{29}Si NMR, and SEM/EDX. The thermal and mechanical characteristics of the POE compounds did not significantly change with an increasing *m*-EPDM content irrespective of the cross-linking state. Interestingly, the adhesion strength to the glass substrate increased linearly with an increasing *m*-EPDM content until 9 phr. Also, the POE compounds containing more than 12 phr *m*-EPDM showed cohesion failure of the encapsulant layer, remaining as a residue of the encapsulant layer on the glass surface after peel testing. The damp-heat test was conducted to evaluate the long-term durability of the photovoltaic module encapsulated with *m*-EPDM, and no significant power loss was found even after 1000 h under the test conditions.

INTRODUCTION

To operate photovoltaic (PV) modules for a lifetime of more than 20 years, a high-quality encapsulant (also known as an encapsulation material) with long-term durability must be selected.^{1–5} It acts as an adhesive or sealant between the top glass and crystalline silicon cells with metalization on the front and rear. In addition, it protects electrical components from corrosive environmental factors to prevent PV module degradation, such as delamination, corrosion, and discoloration.⁶

Because of the demanding requirements mentioned above, only a few polymeric materials have been suggested as encapsulants. The most popular polymeric encapsulation materials include ethylene vinyl acetate (EVA),^{7–13} silicone resin,^{14–20} polyvinyl butyral (PVB),^{21,22} ionomers,^{23–25} thermoplastic polyolefins (TPO),²⁶ and polyolefin elastomer (POE).^{13,27}

Among these, EVA has been widely applied as an encapsulation material for more than 30 years owing to its low cost, high flexibility, and good optical transmittance.^{6,28,29} However, there are still some problems to be solved with the PV encapsulation of EVA films because EVA can trigger the formation of volatile organic compounds (VOCs) during the cross-linking process, which accelerate the degradation of the encapsulant in the PV module for field operation.^{6,7} In addition, its water absorption generates and accelerates acetic acid *via* the chemical reaction with the acetate moiety of the

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EVA backbone, accelerating the failure of PV modules.^{30–34} Thus, alternative polymers should be sought to replace EVA.

Recently, hydrocarbon-based polyolefin elastomers (POEs) have been considered as a new polymeric encapsulation material for PV modules owing to their lower potential-induced degradation (PID) compared to that of EVA.^{2,13} Thus, polyolefin encapsulation materials will offer great market prospects over the next decade. However, because POEs are obtained *via* the copolymerization of ethylene and higher α -olefins using the metallocene catalyst,^{35–38} their poor adhesion to the top glass substrate in a PV module has remained a bottleneck for the development of POE encapsulants. Therefore, the adhesion strengths of POEs to glass must be enhanced to make them encapsulation materials. Despite being on the market for several years, only one study³⁹ has been performed on the incorporation of an adhesion promoter into POE to realize long-term reliability during the operation of PV modules.

In this study, we selected and modified the ethylene–propylene–diene terpolymer (EPDM) as an adhesion promoter, which was compounded with a neat POE to improve their adhesion strength to the glass substrate. For this purpose, EPDM was chemically modified with 3-mercaptopropyltrimethoxysilane (MPTS) *via* a simple thiol–ene click reaction. The expected POE compound series containing the cross-linking agent, dicumyl peroxide (DCP), were prepared using a secondary master batch process. Here, the physical properties of POE encapsulant films were tested to determine the applicability of POE encapsulants to PV modules in crystalline silicon-based solar cells.

EXPERIMENTAL SECTION

Materials. POE (ENGAGE 8137; density: 0.864 g/cm³; MFI: 13 g/10 min) was obtained from Dow Chemical Co. (Midland, MI, USA). EPDM (KEP330, ENB content: 7.9 wt %, ethylene content: 57 wt %) was generously donated by Kumho Polychem (Seoul, Korea). Dicumyl peroxide (DCP) and 3-mercaptopropyltrimethoxysilane (MPTS) were purchased from Sigma-Aldrich, Inc. (Milwaukee, WI, USA). Other organic solvents and chemicals were purchased from Duksan Company (Ansan, Gyeonggi-do, Korea). The solar cells (multicrystalline silicon cells, p-type, 200 μ m-thick, 13.5 \times 14.0 cm in size) used in this study were purchased from Hae Sung Solar Co., Ltd. (Gimpo, Korea).

Synthesis of *m*-EPDM. The thiol–ene click reaction was conducted *via* the grafting reaction on EPDM using MPTS. First, 20 g of EPDM was dissolved in toluene (200 mL); consequently, 2 g of MPTS was added to the mixture. The mixture was stirred until complete dissolution of solutes in a nitrogen atmosphere was observed. Next, the mixture was exposed to UV black light (18 W, Philips Co., Netherlands) for 150 min. Finally, the mixture was poured into excess acetone to precipitate the product, which was filtered, washed with cold acetone several times, and then kept *in vacuo* at 60 °C for 1 day to dry completely.

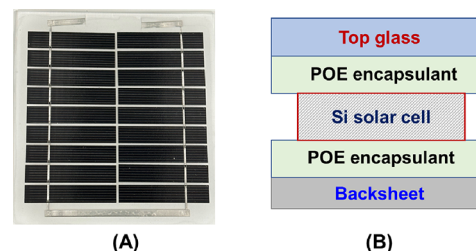
POE Compounding. POE compounds with EPDM and *m*-EPDM were conducted in a batch-type internal mixer (RheoComp system, MKE, Daejeon, Korea) for 8 min at 105 °C with a rotation speed of 50 rpm. In the case of cross-linkable POE compound samples, 2 phr (parts per hundred POE resin) DCP was added to the POE compound during the melt compounding. The *m*-EPDM contents in the POE compounds were controlled as 3, 6, 9, and 12 phr. The

uncross-linked POE compound film was carefully prepared using a manual hot-press apparatus under mild conditions (<110 °C), after which the obtained uncross-linked POE compound film was cured in a manual hot press under 170 °C for 10 min for the instrumental analysis.³⁹

Determination of the Gel Content. The gel contents were determined according to ASTM D2765-16. The cross-linked samples were placed in folded 120-mesh copper screen cages, and their weights were measured before immersion in xylene. The sample was placed in xylene and refluxed for 8 h. The residue specimens were washed with hot xylene several times, vacuum-dried at 120 °C for 3 days, and subsequently reweighed.

Lamination Process for Preparing the PV Module. Encapsulant laminator curing was performed using an automatic laminating machine (YDS-0707, Radiant Automation Equipment Co., Ltd.; Qinhuangdao, China) for 18-cell multicrystalline solar-cell-based PV modules. The detailed procedure and conditions of the lamination process were as follows: The lamination was done at 140 °C and a pressure of 100 kPa for 300 s in the laminator. Then, the pressure on top of the sample was sequentially reduced to 90 kPa and kept for 30 s and then to 55 kPa for 30 s. Thereafter, the pressure was reduced to 25 kPa and kept for 600 s and was finally vented to atmospheric pressure. The stack structure of the PV modules was polyolefin-based backsheet/encapsulant/silicon solar cell/encapsulant/glass (Scheme 1).

Scheme 1. Camera Image of the Test PV Module (A) and Its Laminate Structure Diagram (B)



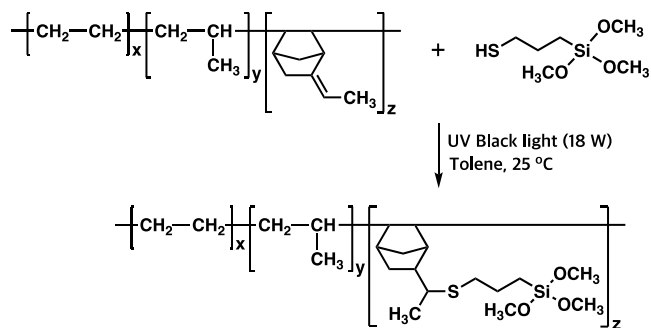
Equipment and Experiments. Nuclear magnetic resonance (NMR) was performed on an Agilent 400 MHz NMR magnet spectrometer (Agilent Technologies, Inc., Santa Clara, CA, USA) using chloroform-*d*₁ (CDCl₃) as a solvent. Transmittance spectra were recorded in the wavelength range of 250–800 nm using a SINCO S-3100 UV/vis spectrophotometer (SINCO, Seoul, Korea). The thermal analysis was measured using a DSC 1 differential scanning calorimeter (Mettler Toledo Co., Greifensee, Switzerland) under a nitrogen atmosphere. The samples were quickly heated to 120 °C, held for 2 min to destroy anisotropy, and then cooled to –75 °C at a rate of 20 °C/min to analyze the recrystallization behavior. Afterward, the crystallized sample was reheated to 120 °C at a rate of 20 °C/min again to analyze the melting behavior. The morphological study of the POE compounds was examined by a JSM-7100F FE-SEM (Jeol, Japan) at 10 kV. The chemical composition of the *m*-EPDM surface was analyzed using EDX (energy-dispersive X-ray; Oxford Instruments) attached to the FE-SEM. Tensile tests (ASTM D412) were performed using an Instron universal testing machine (model 6800; Instron Co., Norwood, MA, USA) equipped with a 1 kN load cell, and measurements were

conducted at a constant crosshead speed of 500 mm/min. The tests were evaluated from the averages of at least five parallel tests. The peel strength measurement was conducted using an ASTM 3330M method at a separation angle of approximately 180° and a separation rate of 150 mm/min at 25 °C. The detailed treatment is described in the literature.³⁹ The characteristics of the encapsulated PV modules were measured using a Newport solar simulator (Newport Corp., Irvine, CA, USA). The current–voltage (I – V) characteristics were determined using a digital source meter (Keithley 2400, Keithley Instruments, Inc., Solon, OH, USA) under standard testing conditions (irradiance of 1000 W/m² with an AM 1.5 G spectrum at room temperature). Damp-heat exposure was conducted under no light, 85 °C, and 85% relative humidity (RH) (85/85 test) for 1000 h.⁴⁰

RESULTS AND DISCUSSION

The bonding strength between the POE encapsulant film and the other components of the PV modules is a very important factor in determining their long-term durability. However, it is difficult to bind the POE-based film and the glass substrate for a long time because the POE is a nonpolar polymer while glass is a polar inorganic material with a smooth surface. Therefore, to achieve strong bonding between them, we designed a new organic additive that can promote the adhesion of the POE encapsulant to the glass substrate. The additive, *m*-EPDM, used in this study is an EPDM grafted by silane coupling agents because the grafting of silane coupling agents can improve the adhesion strength to the other components of PV modules, as well as the glass substrate.⁴¹ Also, to obtain *m*-EPDM under milder conditions, the light-mediated thiol–ene click reaction^{42,43} was conducted using MPTS (Scheme 2). ¹H

Scheme 2. Synthetic Scheme of *m*-EPDM under Thiol–Ene Click Reaction Conditions



NMR measurements were performed to confirm the grafting of MPTS to EPDM, and the obtained spectra are presented in Figure 1A. On the ¹H NMR spectrum of the neat EPDM, the typical resonances of the aliphatic CH, CH₂, and CH₃ units were detected at δ = 0.5–1.7 ppm, and the proton bound to a carbon comprising a double bond in the ENB units showed two resonances at δ = 5.3 and 5.1 ppm in a 3:1 ratio, reflecting the *E*:*Z* conformation ratio of the methyl group in the ENB unit. After the thiol–ene click reaction, the distinctly isolated chemical shift was detected at δ = 3.56 ppm, assigned to the three methoxy (–OCH₃) groups from the MPTS moiety in addition to the expected signals for the neat EPDM. Figure 1B shows the ²⁹Si NMR spectrum for *m*-EPDM, and a new single resonance peak was detected at δ = –42.0 ppm attributed to the silicon atom of the alkyl trimethoxysilane [C–Si(OCH₃)₃]

group. The SEM/EDX analytical method was applied to verify the presence of silicon elements on the *m*-EPDM film, which indicates the chemical modification of the neat EPDM with MPTS. The SEM micrograph, EDX spectrum, and silicon element mapping image for *m*-EPDM are shown in Figure 2. On the mapping image (inset image of Figure 2A), a wide-spreading bright spot over the background indicated that the silicon element was widely and evenly distributed across the *m*-EPDM surface. Although the intensity of the silicon peak (1.75 keV)⁴⁴ was low (Figure 2B), the result suggested that siloxane moieties were distributed evenly on *m*-EPDM. Based on the ¹H NMR, ²⁹Si NMR, and SEM/EDX results, we concluded that the grafting reaction of MPTS to the neat EPDM was performed successfully.

To clarify the thermal behavior of POE compounds depending on the addition amount of *m*-EPDM, DSC thermograms were recorded during cooling and second heating, and their results are listed in Table 1. For the cooling scan, the peak maximum (T_c) of uncross-linked neat POE was detected at 36.3 °C. Meanwhile, the T_c of the POEs did not change much with an increasing *m*-EPDM content. On the second heating DSC scan, the uncross-linked neat POE showed one melting peak (T_m) induced from the melting of monoclinic crystals⁴⁵ measured at 64.0 °C. Also, the melting temperature of the POE compounds was similar to that of the neat POE. These results mean that adding *m*-EPDM into the POE matrix did not significantly impact the second heating thermogram shape and the shifting of the exothermic peak. However, when the neat POE and its POEs compounded with *m*-EPDM were cross-linked, they showed different thermal behavior compared with the uncross-linked counterparts. As shown in Table 1, their T_m and T_c values were lower than those of the uncross-linked samples. These phenomena might be attributed to the increased content of shorter crystallizable chain blocks and the crystal regions surrounded by the cross-linked amorphous region in the POE matrix, respectively.^{46,47} The glass transition temperature (T_g) of the neat POE was detected at approximately –53.3 °C, and the T_g values of its compounds were detected at a similar temperature because *m*-EPDM and POEs have similar T_g values.⁴⁸ Meanwhile, the T_g values of all samples cross-linked using peroxide were detected at a higher temperature than that used to detect the uncross-linked counterparts. In addition, the T_g values of the POE compounds increased with an increasing *m*-EPDM content. It might be attributed to the cross-linking effect and the degree of cross-linking, which disturbs the polymer backbone chain mobility.

To define the degree of cross-linking for the cross-linked samples, their gel contents were measured, and the results are shown in Figure 3. The gel content of the cross-linked samples slightly increased with an increasing *m*-EPDM content. Although the silane coupling agent having a double bond in the POE curing system accelerates its curing reaction and induces a high degree of cross-linking,⁴¹ the increasing degree of cross-linking in this study is related to the existence of an EPDM with free double bonds because this system does not use silane coupling agents with a double bond. Therefore, the silane grafting method on EPDM used in this study is a reasonable pathway to incorporate the coupling agent without any disturbance in the curing process of the POE encapsulant.

The UV/vis spectra were recorded in the transmission mode for the cross-linked film samples of the neat POE and its compounds. The results are presented in Figure 4. All

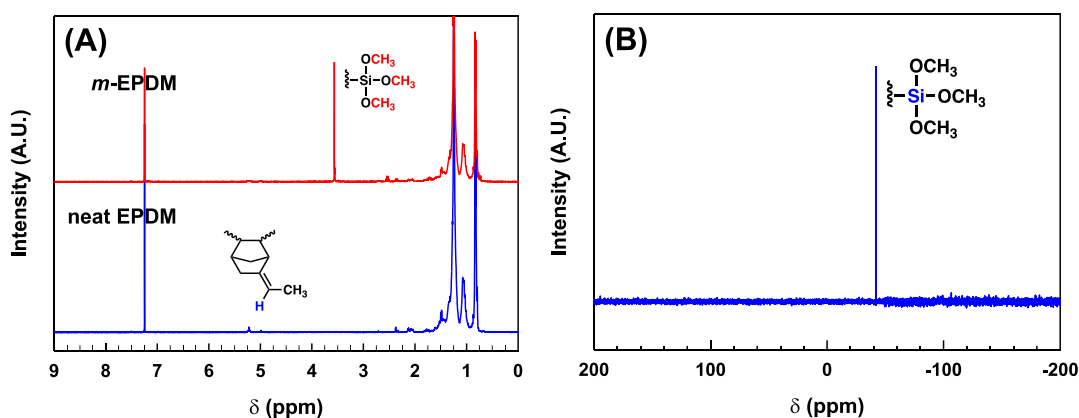


Figure 1. ^1H NMR (A) and ^{29}Si NMR (B) spectra for *m*-EPDM.

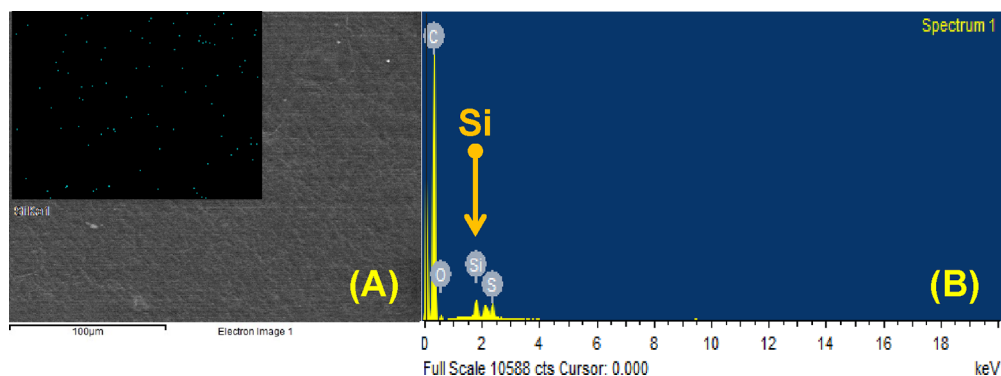


Figure 2. SEM micrograph (the inset shows the silicon element mapping image) (A) and EDX spectrum (B) of *m*-EPDM.

Table 1. Thermal Characteristics of Neat POE and POE Compounds with *m*-EPDM before and after Cross-Linking

<i>m</i> -EPDM content (phr)	before cross-linking			after cross-linking		
	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)
0	-53.3	64.0	36.3	-52.5	60.0	32.7
3	-53.2	64.4	36.2	-53.7	60.4	32.7
6	-52.3	64.0	35.1	-52.2	61.0	33.0
9	-53.3	62.9	36.1	-50.8	61.0	33.0
12	-52.4	63.1	36.0	-49.8	61.8	32.3

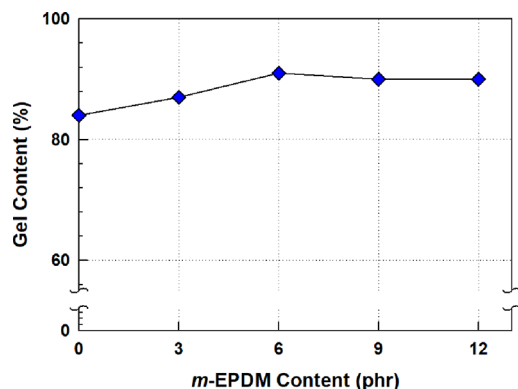


Figure 3. Gel content of the cross-linked neat POE and POE compounds with *m*-EPDM.

compound film samples showed a similar curve pattern to that of neat POE, which blocked the radiation under 250 nm and showed a transmittance of nearly 20%. Generally, the

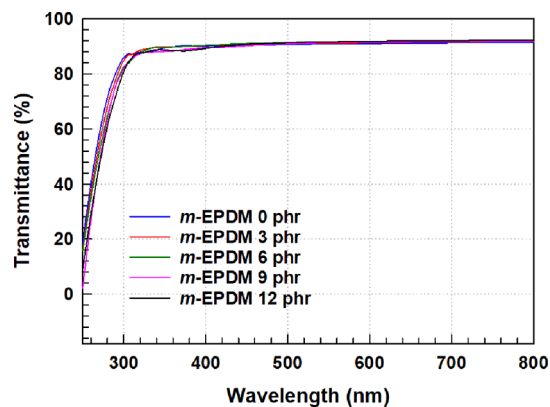


Figure 4. UV/vis light transmittance of the cross-linked neat POE and POE compounds with *m*-EPDM.

commercial polymeric encapsulation material, which was formulated with a UV blocker, has a UV cutoff wavelength below 300–400 nm at a low transmittance of less than 10%.⁴⁹ Unfortunately, this POE encapsulant requires the addition of a UV blocker to be applicable to PV modules. Furthermore, the cross-linked neat POE as well as its compounds transmitted more than 90% light effectively from 400 to 800 nm, which had a transmittance similar to that of EVA.

The mechanical behavior between the uncross-linked and cross-linked POE films was characterized using tensile tests, and the results are presented in Figure 5. According to the literature,⁵⁰ the addition of a small amount (10 wt %) of EPDM into the POE matrix does not significantly affect to the instinctive mechanical properties of the uncross-linked and

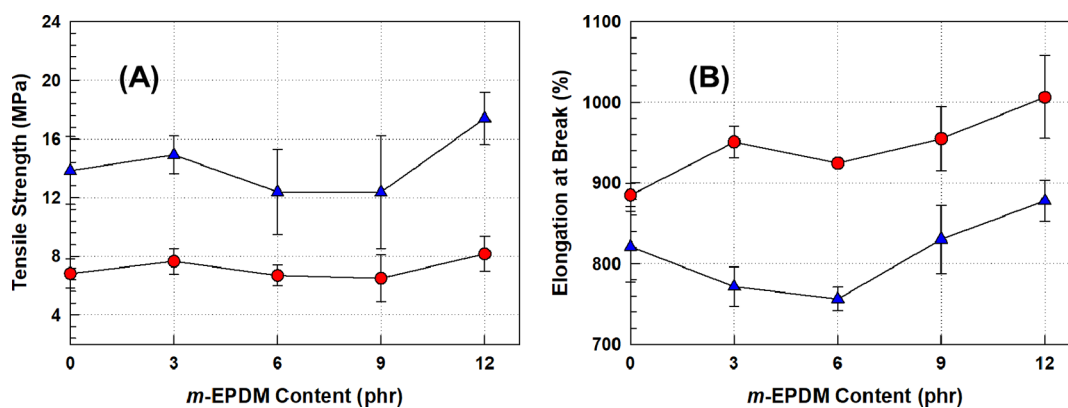


Figure 5. Tensile strength (A) and elongation at break (B) behaviors of the neat POE and POE compounds with *m*-EPDM before and after cross-linking (circles, uncross-linked samples; triangles, cross-linked samples).

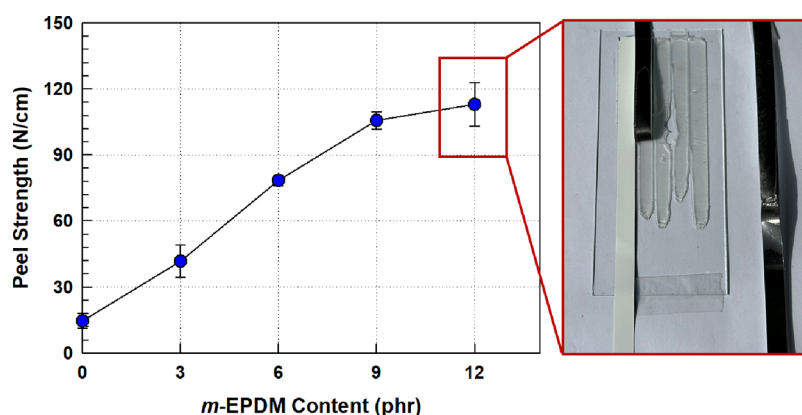


Figure 6. Peel strength of the cross-linked neat POE and POE compounds with *m*-EPDM.

cross-linked compounds. In the case of uncross-linked film samples, the remarkable changes in ultimate properties were not detected with an increasing *m*-EPDM content. These results matched well with the previous results. When those film samples were cross-linked, their tensile strength values showed higher than those of the uncross-linked film samples, but their elongation at break values decreased. This result further proves that the addition of *m*-EPDM into the POE matrix and their dynamic cross-linking improve the mechanical properties of the POE as a photovoltaic encapsulant.

According to ASTM 3330M, the 180° peel test was conducted using a universal testing machine to obtain the adhesion strength between the glass substrate and the encapsulant film. To apply the encapsulation material to the PV module with improved durability, enhancing the peel adhesion strength must be considered. Whenever commercial encapsulation materials are tested, the profile of peel testing shows the fluctuation pattern owing to the uneven peeling path between the encapsulant and the glass substrate.^{33,51} In this study, the estimated peel adhesion strength was taken from the mean of five repetitive peel testing results.^{34,52} As shown in Figure 6, the obtained average adhesion strength of the neat POE film was 14 N/cm, which is too low for a PV encapsulant compared with the commercial EVA encapsulant (adhesion strength, 80–100 N/cm^{49,52}). Since the silane moieties can help to enhance the adhesion strength to the glass substrate,^{6,53,54} we conducted the thiol–ene click reaction between the neat EPDM and MPTS to construct a silane-grafted EPDM (*m*-EPDM); then, the POE was compounded

with *m*-EPDM. This strategy obviated the need for an additional grafting of silane moieties during the lamination process. With increasing *m*-EPDM contents until 9 phr (parts per hundred resin) in the POE compounds, the adhesion strengths increased linearly, indicating that *m*-EPDM modified with silane moieties played a role as an adhesion promoter to the glass substrate. When the amount of *m*-EPDM in the POE compound increased until 12 phr, the peel test result had a similar value with the POE compound containing 9 phr *m*-EPDM. However, the POE compound film remained on the glass substrate after finishing the peel test. It can be interpreted that the adhesion strength of the POE compound containing more than 12 phr *m*-EPDM to the glass substrate was much stronger than the cohesion strength of the POE compound. These results support that the adhesion strength improved using *m*-EPDM can help to prevent moisture diffusion, which occurs owing to interfacial debonding/delamination, hence improving the reliability of PV modules.

To evaluate the longevity of PV modules installed outdoors, the damp-heat test is performed as an accelerated testing method at high levels of temperature and humidity in PV research because the accelerated conditions can affect the interfacial adhesion mechanism (e.g., mechanical interlocking, chemical bonding, molecular interfacial diffusion, and polar–polar interaction). To conduct the damp-heat test, we fabricated PV modules encapsulated using the POE compound containing *m*-EPDM, and the testing was conducted at 85 °C and 85% RH for 1000 h, as per the IEC-61215 recommendation. The *I*–*V* curves of the PV modules

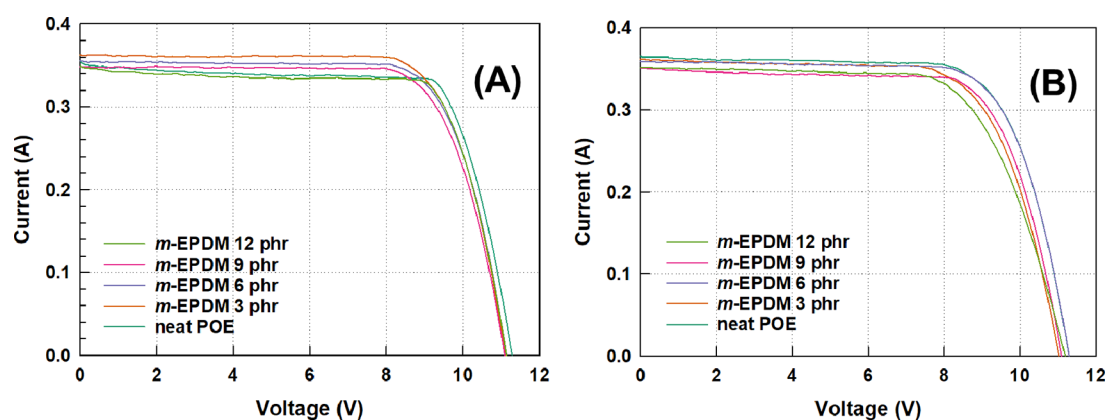


Figure 7. I – V curves of the test PV module before (A) and after (B) 1000 h of the damp-heat test.

Table 2. I – V Parameters of the Test PV Modules Encapsulated with the Cross-Linked Neat POE and POE Compounds with m -EPDM

m -EPDM content (phr)	before the damp-heat test					after the damp-heat test				
	J_{sc} (mA/cm ²)	I_{sc} (mA)	V_{oc} (V)	FF (%)	PCE (%)	J_{sc} (mA/cm ²)	I_{sc} (mA)	V_{oc} (V)	FF (%)	PCE (%)
0	2.37	355.3	11.3	74.7	20.0	2.43	364.8	11.3	72.2	19.8
3	2.42	362.6	11.1	70.4	18.9	2.41	361.6	11.1	70.2	18.6
6	2.32	348.2	11.1	74.4	19.2	2.34	350.6	11.1	72.7	18.9
9	2.36	354.5	11.1	75.3	19.7	2.39	359.0	11.3	73.2	19.8
12	2.33	349.1	11.1	70.9	18.3	2.34	351.3	11.2	68.3	17.8

encapsulated by using the neat POE and POE compounds with m -EPDM are shown in Figure 7. From the I – V curves, the fill factor (FF) and power conversion efficiency (PCE) values were calculated, and the results are listed in Table 2. The initial PCE values of the PV modules fabricated using the neat POE or POE compounds ranged from 18.3 to 20.0%. There was no significant power drop (less than 5%) after 1000 h of the damp-heat test for the PV modules. Consequently, the addition of m -EPDM could help to enhance the creep resistance of POE and plays an important role in the thermal stability of PV modules under different conditions.

CONCLUSIONS

In this study, a POE encapsulation material designed for PV modules was successfully prepared by compounding it with a newly modified EPDM *via* a simple thiol–ene click reaction. The constructed POE compounds showed thermal characteristics similar to that of neat POE after the addition of m -EPDM until 12 phr. After cross-linking the neat POE and its compounds, their recrystallization temperature (T_c) and melting temperature (T_m) were depressed down owing to the interruption of polymer chain mobility. However, they did not show significant differences regardless of the amount of m -EPDM. In addition, with an increasing m -EPDM content in the POE compounds, their transmittance was more 90%. The cross-linking reaction of the neat POE and POE compounds affected their tensile properties compared to those of the uncross-linked neat POE and POE compounds. However, the addition of m -EPDM in the neat POE was independent of their tensile properties even cross-linked or uncross-linked thereof. Until the addition of m -EPDM at 9 phr, the peel strength increased linearly, and the encapsulant was peeled off from the glass substrate. However, the addition of more than 12 phr did not increase the adhesion strength of the encapsulant, and the encapsulant remained as a residue on

the glass substrate. The damp-heat test results showed no significant power drop after 1000 h under the test conditions. Finally, m -EPDM medicated by a simple thiol–ene click reaction could provide an alternative strategy to improve the adhesion strength of an encapsulation material for the development of high-quality PV modules with long-term durability.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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