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Study of the Application of Polyolefin Elastomer (POE) Grafted Silane Coupling Agent in Photovoltaic Encapsulation Adhesive Film

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Abstract: POE-g-KH-171 was prepared by twin-screw melt extrusion method, and the differences in the properties of POE-g-KH-171 prepared by using polyolefin elastomer (POE) as the substrate, different contents of DBPH, and different contents of coupling agent were explored. The grafting products were characterized qualitatively by Fourier infrared (FT-IR) spectroscopy, and the graft ratio and grafting efficiency of the products were determined. The performance of the adhesive was analyzed by a 180° peel strength test. The optimal content of vulcanizing agent was found to be 0.25, with the content of silane coupling agent KH-171 being 4. This composition achieved a graft ratio of 3.4, a grafting efficiency of 0.85, and a melt flow index of 12.98 g/10 min; the adhesion performance was excellent. The mobility of the product that was created with the optimum ratio of materials was then tested, followed by a comparative analysis with POE. The modified material (POE-g-KH-171) showed better performance than regular POE. Besides, POE-g- KH-171 had similar properties with ethylene-vinyl acetate (EVA) materials. This modified material is expected to mature in the future, contributing to the advancement of photovoltaic encapsulation technology.

Keywords: Silane coupling agent KH-171; POE; Tensile strength; Breaking strength

1. Introduction

Photovoltaic (PV) encapsulation materials are a very important part of a PV module. These materials should protect the electrical components from the external environment and ensure electrical insulation so that the module can function normally [1]. However, encapsulation materials are prone to degradation due to factors like temperature, humidity, and radiation exposure, leading to delamination, corrosion, and discoloration [2].

Recent decades have seen a series of changes in the choice of encapsulant materials for PV, from polydimethylsiloxane (PDMS) in the earlier days to ethylene vinyl acetate (EVA) for glass backsheets and polyvinyl butyral (PVB) for glass modules in recent years [3,4]. The degradation of EVA leads to the production of acetic acid and polyenes, as well as acetaldehyde and other gases such as CO, CO_2, and CH_4 [5,6]. The main cause of degradation of PV modules is the acetic acid produced, which corrodes the internal structure of the cell [7-9].

With the recent research on new PV encapsulation materials, new formulations developed to overcome the problems arising from the use of EVA have been tested. Thermoplastic polyolefins (TPO) and polyolefin elastomers (POE) have been tested and introduced as alternatives to EVA for encapsulants used in PV applications [10-14]. POE does not have vinyl acetate molecules in its structure and does not produce acetic acid when it degrades. In this work, we modified the POE material using a silane coupling agent. The properties and performance of the materials were tested through various experiments. The adhesive film was created through the casting method and bonded to the glass plate. The tensile strength machine was used to test the adhesive properties of the material.

2. Materials and methods

2.1. Experimental materials

Three commercially available polymeric materials were used for this study

(1) Industrial grade silane coupling agent (KH-171): A-171 (GE, USA), KBM-1003 (Shin-Etsu, Japan), Z-6300 (Dow Corning, USA).
(2) Polyolefin elastomer (POE), DuPont (Nanjing Jingtianwei Chemical Co. Ltd.) (3) (3) 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane (DBPH) (Shanghai Jiji Biochemical Technology Co.)

2.2. Experimental equipment

(1) Pharma16 Twin Screw Extruder (Nanjing Dalit Machinery Co., Ltd)
(2) Nicolet iS20FT Fourier-Transform Infrared Spectrometer (FT-IR) (Thermo Fisher Scientific, USA)
(3) Electric Heating Constant Temperature Blast Drying Oven (Guangdong Hongzhan Science and Technology Co., Ltd),
(4) Pelletizing Machine (Nanjing Ruihua Mechanical and Electronic Co., Ltd)
(5) Melt Flow Rate Analyzer (Songshu Testing Instruments Co.)
(6) Electronic Universal Tensile Tester (High Speed Rail Testing Instrument Co.)

2.3. POE-g-KH-171 preparation

The silane coupling agent KH-171, POE, and DBPH were mixed according to the ratios specified in **Table 1**. The mixture was then stirred into a high-speed mixer until evenly dispersed. Subsequently, the thoroughly mixed mixture was added to a twin-screw extruder for melt extrusion. After extrusion, the material was granulated using a pelletizer to obtain POE-g-KH-171. The temperature settings for the twin-screw extruder were as follows: 170°C, 175°C, 180°C, 190°C, 190°C, 180°C, 175°C, 170°C, with a starting temperature of 170°C. The melt pressure was maintained at 2 MPa, the screw speed was set to 500 r/min, and the feed rate was 110r/min. After cooling and pelletizing, the material was dried in an oven at 130°C for 4 hours to produce POE-g-KH-171 with the serial numbers shown in **Table 1**.

Table 1

Serial number	Amount added/part			
	POE	KH-171	DBPH	Antioxidant-168
$L_0\backslash K_0\backslash T_0\backslash Y_0\backslash R_0$	100	1/2/3/4/5	0	0.2
$L_1\backslash K_1\backslash T_1\backslash Y_1\backslash R_1$	100	1/2/3/4/5	0.05	0.2
$L_2\backslash K_2\backslash T_2\backslash Y_2\backslash R_2$	100	1/2/3/4/5	0.1	0.2
$L_3\backslash K_3\backslash T_3\backslash Y_3\backslash R_3$	100	1/2/3/4/5	0.15	0.2
$L_4\backslash K_4\backslash T_4\backslash Y_4\backslash R_4$	100	1/2/3/4/5	0.2	0.2
$L_5\backslash K_5\backslash T_5\backslash Y_5\backslash R_5$	100	1/2/3/4/5	0.25	0.2
$L_6\backslash K_6\backslash T_6\backslash Y_6\backslash R$	100	1/2/3/4/5	0.3	0.2

2.4. Characterization

(1) Structural characterization

The sample to be tested was dried in a drying oven at 85℃ for 10 h and then put into a plate vulcanizing machine, and then pressed into a sheet at 180℃ for 5–8 min. A sample was then taken from the sheet to run an FT-IR test at 4000–500 cm^{-1}.

(2) Determination of graft ratio

0.5 g of purified grafted polymer was added into a three-necked flask containing 80 mL of xylene. The three-necked flask was heated on a heating mantle to dissolve the polymer. The mixture was then refluxed for 30 min, and 10 mL of trichloroacetic acid-isopropanol standard solution was slowly added throughout the process. The reflux was stopped after 1.5 h. Phenolphthalein was added as an indicator, and the solution was titrated with potassium hydroxide in ethanol. The titration was performed 3 times and the average value was used to calculate the grafting ratio. The graft ratio was calculated according to the formula below.

$$G = \frac{C_1V_1 - C_2V_2 \times M}{W \times 1000} \times 100\%$$

C_1 (unit: mol/L) denotes the concentration of trichloroacetic acid-isopropanol solution and V_1 (unit: mL) denotes the volume used; C_2V_2 denotes the concentration of potassium hydroxide-ethanol solution (unit: mol/L) and V_2 (unit: mL) denotes the volume used; M is the molecular mass DBPH (209 g/mol); W denotes the mass of purified graft polymer weighed (g).

(3) Calculation of grafting efficiency: The grafting efficiency in this experiment represents the ratio of the mass of monomer DBPH involved in the grafting reaction to the mass of monomer DBPH added to the reaction. The formula for the grafting efficiency is as follows:

$$E = \frac{G \times W}{W_1} \times 100\%$$

G denotes the graft ratio, W denotes the mass of purified grafted polymer weighed (g) and W1 denotes the mass of monomer DBPH added for the reaction (g).

(4) Peel strength

The POE-g-KH-171 prepared by casting method was cut into a rectangular pieces of 10cm × 3cm length. The vulcanizing agent was added and the pieces were flattened. They were pressurized at 150℃, 1 MPa, for 20 min.

The mold was then taken out and left to cool for 12 h. A 180° peel test was then carried out according to GB/T 2792-1998 standards with a tensile rate of 300 mm/min. The peak value of the tension was recorded; the peel test was repeated 3 times and the average value was obtained.

(5) Measurement of melt flow index

The melt flow index was carried out according to GB/T 3682-2000 standard. The temperature was set to 190 ℃ and the load was set to 2.16 kg. The process was carried out six times and the average melt flow index was obtained.

3. Results and discussion

3.1. FTIR

As shown in **Figure 1**, the C=C vibrational peaks at 2920 cm^{-1} and 1470 cm^{-1} are the characteristic peaks belonging to POE. The pure POE-g-KH-171 showed a strong absorption peak at 1092 cm^{-1}, which was caused by the antisymmetric stretching of Si-O-Si bond, thus proving that the silane coupling agent was successfully grafted onto the polymer chain of POE. The silane coupling agent decomposed under the experimental conditions to generate free radicals, which cross-linked with alkene polymers, thus improving adhesive properties of alkene polymer.

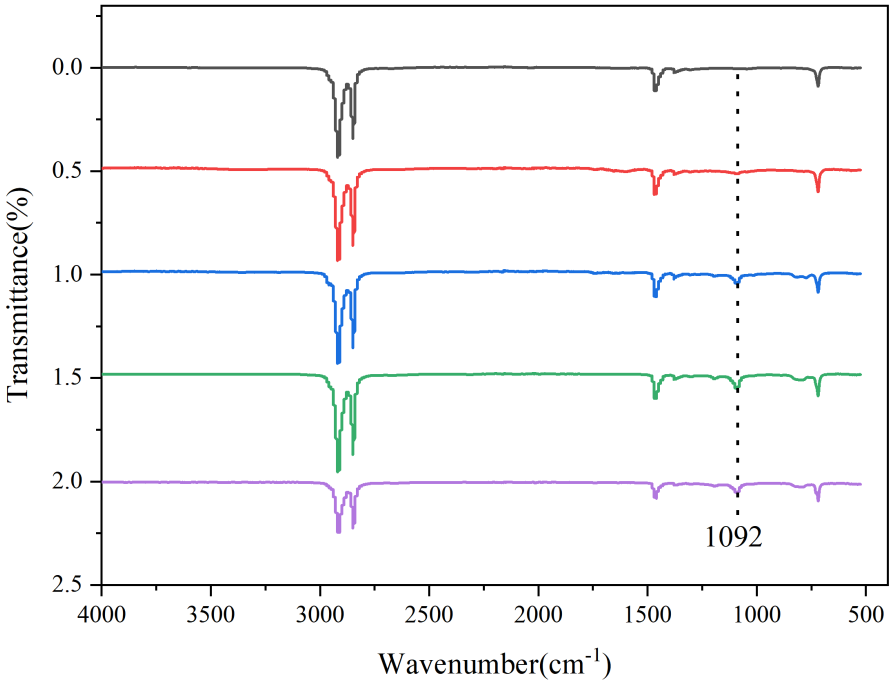

Figure 1. IR spectra of POE-g-KH-171 with different graft ratios

3.2. Analysis of factors affecting the bonding performance of POE-g-KH-171

3.2.1. Graft ratio of POE-g-KH-171

Different groups of experimental samples were tested, and the effect of DBPH content on the graft ratio of the product is shown in **Figure 2**.

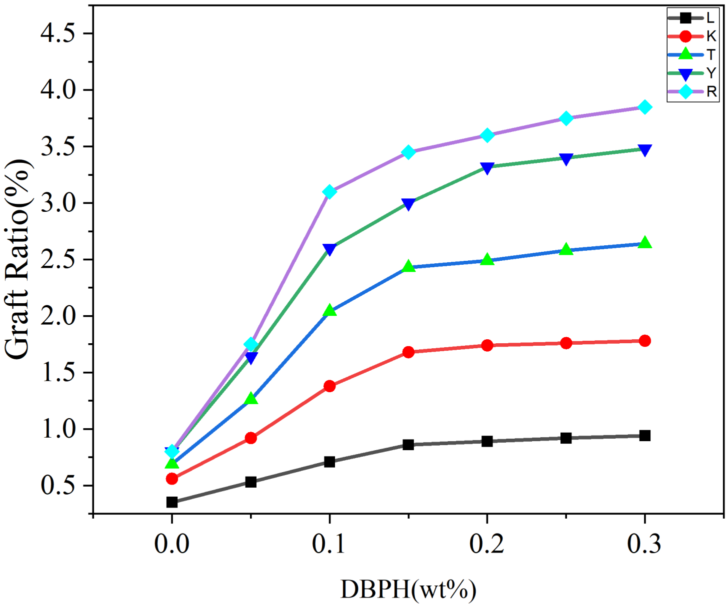

Figure 2. DBPH content versus graft ratio

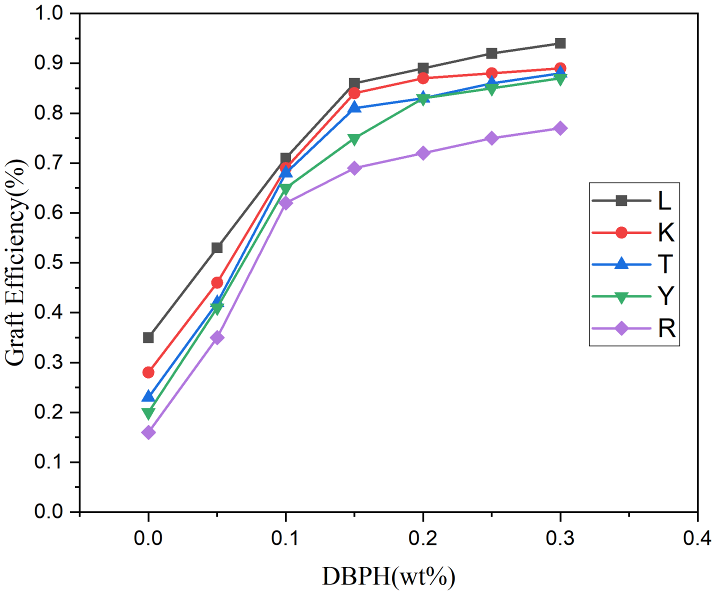

Figure 3. DBPH content vs grafting efficiency

The cross-linking process began with the addition of DBPH, which initiated the grafting reaction. As the amount of DBPH added increased, it reached a saturation point where further addition of DBPH led to local vulcanization reactions (**Figure 3**). These reactions were not conducive to the grafting reaction and ultimately affected the grafting efficiency. In summary, the optimal overall performance was achieved when the amount of DBPH added was controlled at 0.25.

After determining the addition amount of DBPH to be 0.25, further investigation was conducted on the effect of the silane coupling agent on the graft ratio. The silane coupling agent KH-171 was selected for the reaction. The reaction was carried out to obtain the average values of the grafting rate and the content of the silane coupling agent. The effect of the content of the silane coupling agent on the graft ratio are illustrated in **Figure 4**.

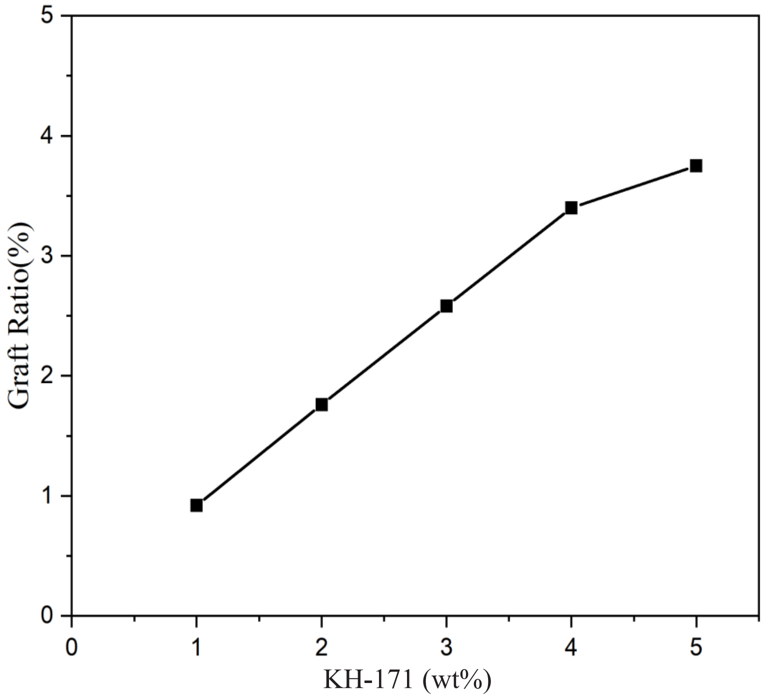

Figure 4. Graft ratio vs. the content of KH-171

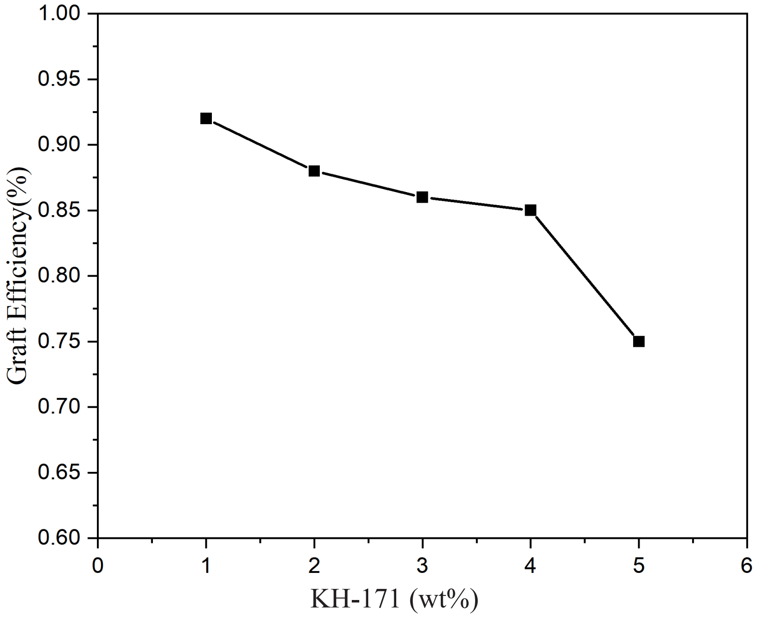

Figure 5. Grafting efficiency vs. KH-171 content

KH-171 was added to the material after treatment. The silane structure would then interact with the POE structure. The silane coupling agent was treated to form silanol groups on the particle's surface [15]. These organic functional groups interacted with the polymer, while the silanol groups formed covalent bonds with the inorganic surface, thereby enhancing the product's interfacial adhesion [16]. As the amount of silane coupling agent added increased, the rate of grafting rate growth decreased, along with a decline in grafting efficiency. The silane coupling agent within the entire POE system reached silicon-oxygen saturation after hitting the optimal reaction critical point, resulting in an excess of functional groups within the system. Despite the increase in molecular weight, the proportion of molecules effectively reacting in the reaction decreased, ultimately leading to a reduction in grafting efficiency.

3.2.2. Melt index of POE-g-KH-171

The effect of the content of DBPH on the melt flow index of POE-g-KH-171 is shown in **Figure 6**.

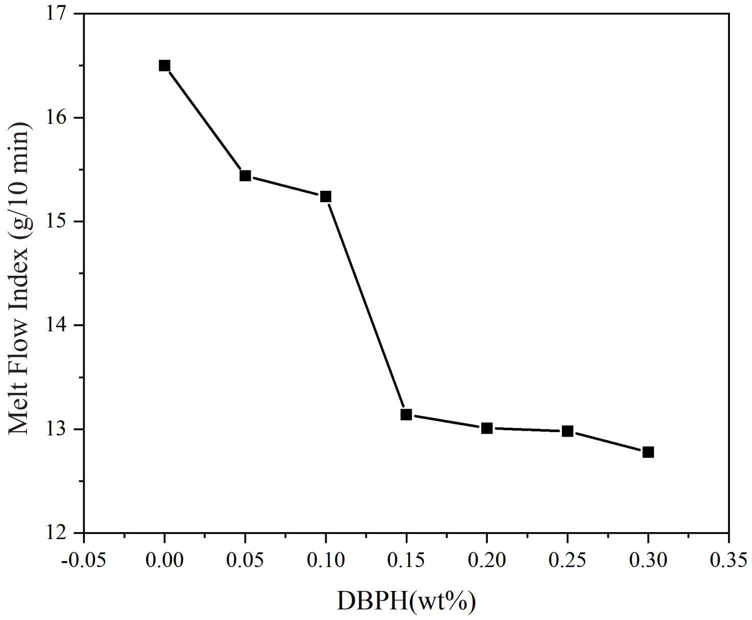

Figure 6. DBPH content vs. melt flow index

The relationship between KH-171 content and the melt flow index of POE-g-KH-171 is shown in **Figure 7**.

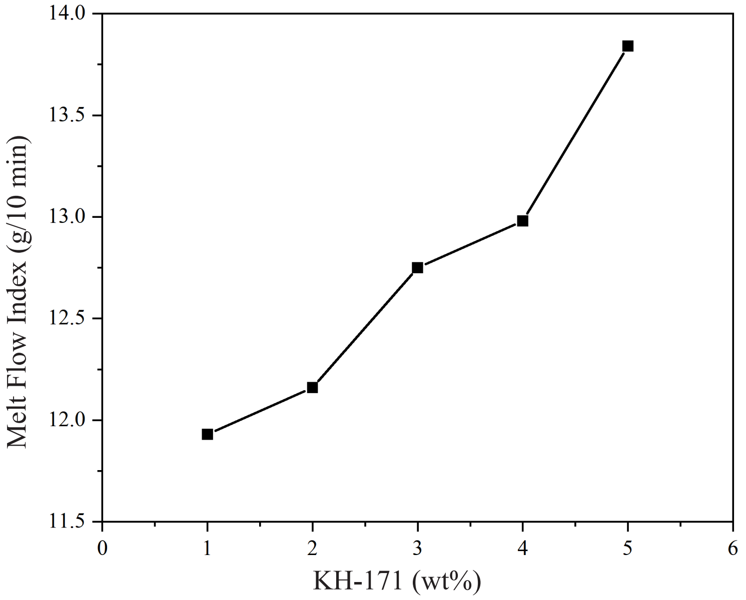

Figure 7. KH-171 content vs. melt flow index

3.3. POE-g-KH-171 bonding performance analysis

3.3.1. Effect of graft ratio and grafting efficiency on peel strength

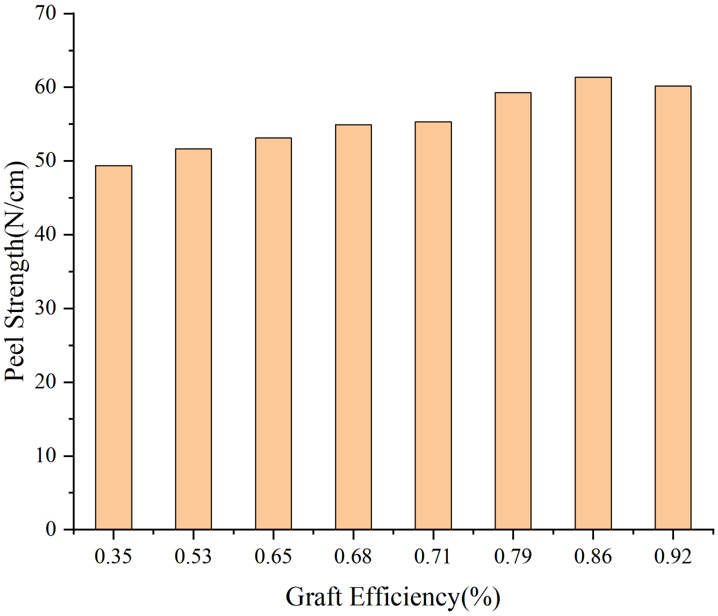

Figure 8. Graft efficiency vs. peel strength

As the grafting efficiency improved, the peel strength of the resulting modified POE gradually increased. However, the growth trend gradually decreased, and the peel strength began to decrease with further increases in grafting efficiency. This phenomenon occurred because the increase in grafting efficiency led to enhanced adhesion of POE-g-KH171 due to the increased polarity resulting from the POE reacting with KH171 and DBPH. However, as the grafting efficiency continued to increase, side reactions also began to increase. Consequently, although the grafting process was completed within the system, the excess silane coupling agent and DBPH weakened the overall adhesion of the system, resulting in a slight decrease in peel strength.

3.3.2. Effect of melt flow index on peel strength

The effect of the melt flow index on the peel strength of POE-g-KH171 is illustrated in **Figure 9**.

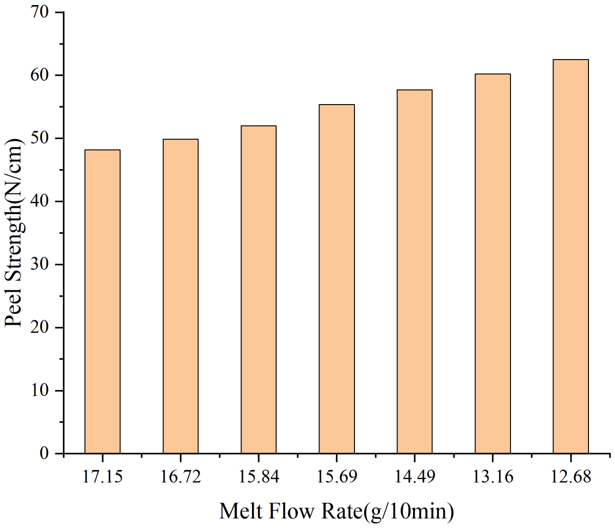

Figure 9 Melt flow index vs. peel strength

The peel strength decreased and the melt flow index increased. This increased mobility led to uneven bonding of the adhesive within the structure, which was not conducive to two-phase bonding and ultimately reduced adhesion For instance, in the case of POE-g-KH-171 with a melt flow index of 12.68 g/10min, it exhibited the highest peel strength. Compared to EVA, which typically has an average peel strength of 59N/cm, POE-g-KH-171 showed comparable peel strength. Moreover, considering performance in various usage environments, such as resistance to acids and alkalis, the modified POE showed more favorable characteristics.

4. Conclusion

(1) POE-g-KH-171, a coupling-agent-grafted POE, was prepared using the twin-screw melt extrusion method. By comparing its FT-IR spectrum with that of POE, it was observed that POE-g-KH-171 exhibited a strong absorption peak at 1092 cm-1, indicating successful grafting of KH-171 onto POE.

(2) Upon testing, it was found that when the initiator DBPH was added at a content of 0.25 and KH-171 was added at a quantity of 4, the graft ratio reached 3.4, with a grafting efficiency of 0.85. Additionally, the melt flow index was measured at 12.98 g/10min, marking the best performance achieved from the comprehensive evaluation.

(3) Utilizing the casting method, the modified POE exhibited a peel strength of 62.51N/cm. With improved polarity, it demonstrated properties akin to EVA, suggesting its suitability for photovoltaic cell encapsulation.

Disclosure statement

The authors declare no conflict of interest.

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