

# Maleic Anhydride Grafted Polyethylene Powder Coated with Epoxy Resin: A Novel Reactive Hot Melt Adhesive

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Received 19 March 2009; accepted 9 October 2009

DOI 10.1002/app.31576

Published online 1 December 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A novel reactive hot melt adhesive was prepared by coating an epoxy resin on maleic anhydride grafted polyethylene (MAPE) powder. This adhesive had markedly improved adhesion power compared with pristine MAPE powder, which is normally used as a hot melt adhesive. The generation of an ester linkage by the reaction between the anhydride group of MAPE and the hydroxyl group of epoxy resin, during the bonding operation at 190°C with the pressure of 22 MPa for 30 min, was confirmed from the FTIR spectra. The bond strength was further improved by a small amount of 1-methylimidazole,

which accelerated the esterification reaction. When the epoxy resin was coated on hydrated MAPE, in which the anhydride group of MAPE was converted into carboxylic acid group by the reaction with water, the esterification reaction was much faster than that of pristine MAPE, and consequently, the bond strength of the adhesive was much higher than that of pristine MAPE coated with epoxy resin. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 328–332, 2010

**Key words:** adhesives; polyethylene; epoxy resin; infrared spectroscopy

## INTRODUCTION

Polyethylene (PE) is one of the most commonly used commodity thermoplastics, because it has good mechanical and thermal properties, and chemical resistance, and is low in cost. However, low surface energy and the lack of reactive sites significantly limit its use in applications requiring good surface/interface properties, such as bonding, printing, and polymer blends. These drawbacks can be overcome by the grafting of polar functional monomers onto the PE backbone. Maleic anhydride (MAH) is one of the most common polar monomers used in free radical initiated grafting, because MAH is not readily polymerized under the conditions employed in grafting reactions and is therefore grafted at high efficiency without the accompanying formation of any homopolymer.<sup>1–5</sup>

Normally the grafting reaction is executed by a solution process or a melt process. The solution process is relatively complex and expensive, because the reaction is carried out in a suitable solvent and the reacted product is precipitated with the aid of a

nonsolvent. The melt process can be conducted in an extruder or internal mixer in a relatively short time without solvent. Therefore, reactive extrusion during the melt state is the most commonly used industrial process. However, it is difficult to remove residual MAH and peroxide.<sup>2,6</sup> In the 1990s, solid phase processes were developed in which PE powder was reacted with MAH dissolved together with peroxide in a small amount of interfacial wetting agent such as xylene. This is an environmentally friendly and cost effective process, because it is accomplished at a relatively low temperature with a small amount of solvent. Furthermore, the reacted powder can be easily washed or modified by coating.<sup>7–9</sup>

In this article, we report that the adhesion power of MAH-grafted PE (MAPE) can be improved substantially so that it can be utilized effectively as a novel reactive hot melt adhesive, when modified by a coating of a small amount of epoxy resin.

## EXPERIMENTAL

### Materials

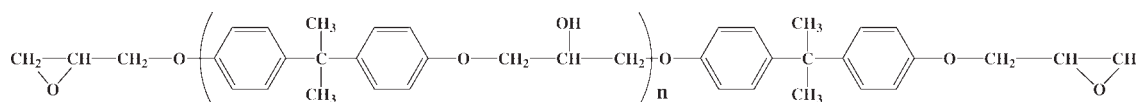
High-density polyethylene powder (volume weighted mean size: 74 μm, M850, Korea Petrochemical Industry, Seoul, Korea), maleic anhydride (MAH, Yongsan Chemicals, Seoul, Korea), benzoyl peroxide (Hanawa Chemical Pure, Osaka, Japan), 1-methylimidazole (MIZ, Tokyo Chemical Industry, Tokyo, Japan), xylene (Aldrich, Milwaukee, WI), acetone (Aldrich), methanol (Aldrich), and benzyl alcohol (Aldrich)

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Contract grant sponsor: Support for Corporate-affiliated Research Institute of Academic-Industrial-Institutional Cooperation Establishment Business.

were used as received. An epoxy resin, glycidyl end-capped poly(bisphenol A-co-epichlorohydrin) (Chemical Structure 1), whose average molecular

weight is 374 (Epoxy-374) and commercial name is YD-128, was supplied from Kukdo Chemical Co. (Seoul, Korea).



Chemical Structure 1

### Modification of PE

To prepare MAH-grafted PE (MAPE), MAH (1.2 g), styrene (1.3 g), and BPO (0.3 g) were dissolved in a mixed solvent of xylene (0.12 mL) and acetone (20 mL). This solution was coated uniformly on PE powder (20 g) in a reactor equipped with an agitator and reacted at 85°C for 8 h under N<sub>2</sub> atmosphere. The reacted product was washed with acetone and dried under vacuum for 12 h.<sup>7</sup>

MAPE was dispersed for 24 h in 20-fold of acetone, in which appropriate amounts of epoxy resin was dissolved, and then acetone was evaporated at room temperature under vacuum to get MAPE coated with epoxy resin (MAPE-EX).

To prepare hydrated MAPE (HMAPE), in which the anhydride group was converted to acid groups by the reaction with water, MAPE (5 g) was agitated in the mixed liquid of acetone (250 mL) and water (200 mL) for 1 day at room temperature and dried under vacuum at 25°C. HMAPE coated with epoxy resin (HMAPE-EX) was made by the same method used in the preparation of MAPE-EX.

### Characterization

The amount of MAH grafted onto PE was determined by chemical titration. The MAPE (0.3 g) was dissolved in xylene (120 mL) at 120°C, and after addition of 0.2 mL of water, the mixture was refluxed for 1 h to convert the anhydride group into carboxylic acid groups. This solution was titrated with 0.025M KOH solution of methanol/benzyl alcohol (1/9 volume ratio), with two drops of 1% phenolphthalein solution in ethanol as an indicator.<sup>8</sup> The amount of MAH grafted on PE was 0.535 ± 0.087 wt %, and melt index of the MAPE measured at 190°C with 2.16 kg load was 0.48 g/10 min.

To evaluate the adhesion power of the MAPE-EX or HMAPE-EX as an adhesive, two aluminum sheets of 40 μm thickness were adhered with MAPE-EX or HMAPE-EX at 190°C under 22 MPa of pressure for 30 min. The thickness of MAPE-EX bonding two aluminum sheets was about 0.065 mm. The bond strength was measured by a 180° peel test with ten-

sile tester (OTU-2, Oriental TM Co.) at a peeling speed of 50 mm/min.

The FTIR spectra of MAPE or HMAPE powders were recorded with an FTS 2000 FTIR (Varian) using KBr tablets that were made by compression molding KBr powder mixed with a small amount of specimen powder. To get the FTIR spectra of the adhesives, adhered films, used for the bonding of two aluminum sheets, were examined.

### RESULTS AND DISCUSSION

The bond strengths between two aluminum sheets adhered by MAPE-EX as an adhesive are given in Table I. When MAPE was coated with Epoxy-374 (Serial number 1–8), the bond strength increased as the coated amount of Epoxy-374 increased; however, it decreased again with higher amounts of Epoxy-374. These results show that the adhesion power of MAPE as an adhesive can be improved significantly by coating with an appropriate amount of epoxy resin.

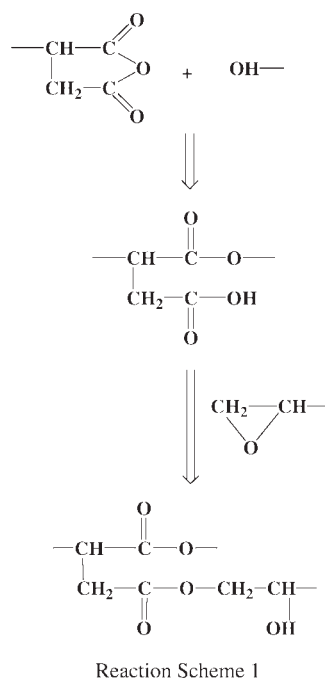
The FTIR spectra of MAPE coated with Epoxy-374, after use as adhesives for the adhesion of two aluminum sheets, are shown in Figure 1. The spectra were normalized with the absorption band at 721 cm<sup>-1</sup> as a reference band. Figure 1(a) shows that MAPE has a sharp symmetric stretching band of the anhydride C=O group at 1784 cm<sup>-1</sup>, and two small asymmetric stretching bands of the anhydride C—O—C group at 956 cm<sup>-1</sup> and 927 cm<sup>-1</sup> due to the grafted MAH.<sup>2,8</sup> As the amount of coated Epoxy-374 is increased, it can be observed in Figure 1 that these peaks are reduced, whereas the new peaks: a symmetric stretching band of the ester C=O group at 1740 cm<sup>-1</sup>, and the stretching band of the epoxide group at 919 cm<sup>-1</sup> and other characteristic bands of Epoxy-374 at 574 cm<sup>-1</sup>, 1510 cm<sup>-1</sup>, and 1607 cm<sup>-1</sup> are increased.<sup>10</sup> These FTIR spectra indicated that ester groups were generated by the reaction between the anhydride group of MAPE and the epoxy group of Epoxy-374 by the following Reaction Scheme 1 during compression at 190°C,<sup>11</sup> and the unreacted excess epoxy groups were increased as the amount of Epoxy-374 was increased. The ratios of peak

TABLE I  
Bond Strength and FTIR Peak Intensity of Adhesives

Serial number	Composition (by weight)				Bond strength <sup>a</sup> (N/m)	FTIR peak intensity ratio, $I_{1740}/I_{1784}$
	MAPE	HMAPE	Epoxy-374	1-Methylimidazole		
1	100	–	–	–	447	–
2	100	–	0.6	–	451	$1.35 \times 10^{-1}$
3	100	–	1.8	–	558	$1.65 \times 10^{-1}$
4	100	–	3.0	–	625	$2.22 \times 10^{-1}$
5	100	–	4.2	–	815	$2.22 \times 10^{-1}$
6	100	–	5.4	–	712	$2.35 \times 10^{-1}$
7	100	–	6.6	–	702	$5.00 \times 10^{-1}$
8	100	–	7.8	–	662	2.25
9	100	–	1.8	0.06	664	3.11
10	100	–	4.2	0.03	888	2.19
11	100	–	4.2	0.06	1134	2.37
12	100	–	4.2	0.12	959	3.03
13	100	–	4.2	0.18	899	3.07
14	–	100	–	–	841	–
15	–	100	1.8	–	1146	$8.40 \times 10^{-1}$
16	–	100	3.0	–	1225	$9.27 \times 10^{-1}$
17	–	100	4.2	–	1066	1.19
18	–	100	5.4	–	1037	1.44
19	–	100	6.6	–	894	2.44

<sup>a</sup> The standard deviations were less than 20 N/m.

intensity at  $1740 \text{ cm}^{-1}$  [ $I_{1740}$ , see Fig. 1(d)] to that at  $1784 \text{ cm}^{-1}$  ( $I_{1784}$ ) shown in Table I also indicate that esterified anhydride group was increased when the amount of Epoxy-374 was increased.



Considering that there are 0.00545 mol of anhydride groups in 100 g of MAPE and there are 0.0225 mol of epoxy groups in 4.2 g of Epoxy-374, our measurements of bond strength (Table I) suggested that an  $\sim$  fourfold increase of epoxy groups was

necessary for optimum bond strength (Serial number 5). However, Figure 1(c), in which the anhydride band at  $1784 \text{ cm}^{-1}$  is evident, indicates that anhydride group is still present with a sufficient amount of available epoxy groups.

MIZ catalyzes the esterification reaction between anhydride and epoxy group.<sup>12</sup> The Serial numbers 9–13 of Table I show that the bond strength is improved when MIZ is coated with Epoxy-374. Figure 2 shows that the decrease of the anhydride

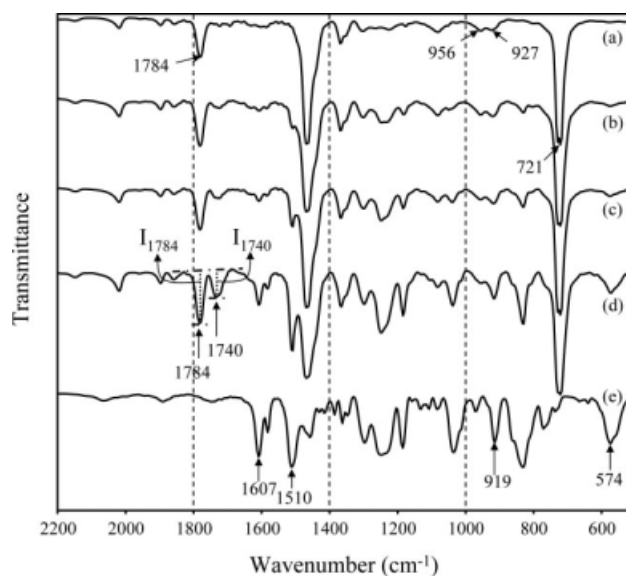
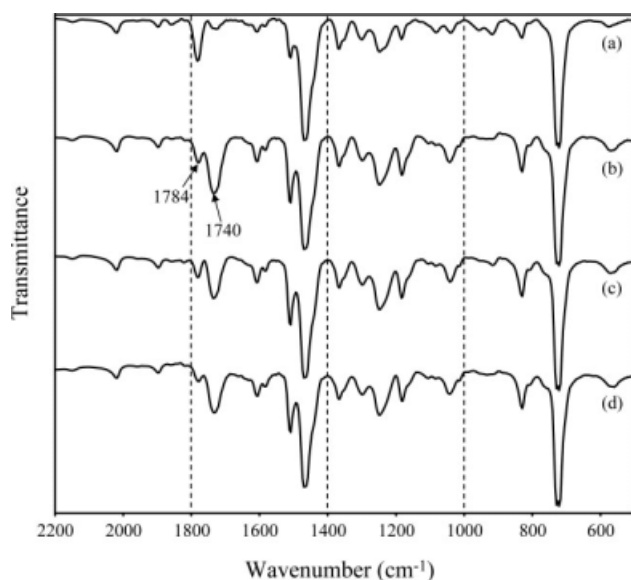


Figure 1 FTIR spectra of the adhesives with the MAPE/Epoxy-374 compositions of (a) 100/0, (b) 100/1.8, (c) 100/4.2, (d) 100/6.6, and (e) Epoxy-374.

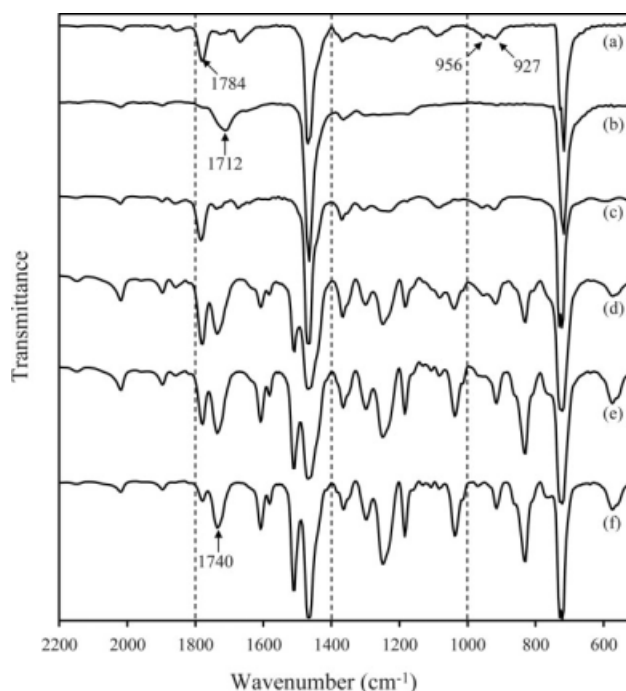
C=O band at  $1784\text{ cm}^{-1}$ , the increase of the ester C=O band at  $1740\text{ cm}^{-1}$ , and the decrease of the anhydride and epoxy group bands at  $910\text{--}960\text{ cm}^{-1}$  are evident even with small amounts of MIZ. These results and  $I_{1740}/I_{1784}$  values in Table I demonstrated that MIZ catalyzed the reaction between the anhydride group of MAPE and the hydroxyl group of Epoxy-374 and that this enhanced reaction improved the bond strength.

One can see in the FTIR spectrum of HMAPE [Fig. 3(b)] a symmetric stretching band of the carboxylic acid C=O group at  $1712\text{ cm}^{-1}$  instead of the characteristic peaks of the anhydride group at  $1784\text{ cm}^{-1}$ ,  $956\text{ cm}^{-1}$ , and  $927\text{ cm}^{-1}$  [Fig. 3(a)]. This indicates that the anhydride group of MAH was converted into carboxylic acid groups by the reaction with water. However, Figure 3(c) shows that the peaks of the anhydride groups at  $1784\text{ cm}^{-1}$ ,  $956\text{ cm}^{-1}$ , and  $927\text{ cm}^{-1}$  appear again when HMAPE was pressed at  $190^\circ\text{C}$  with the pressure of 22 MPa for 30 min to bond two aluminum sheets. These results indicated that two adjacent carboxylic acid groups were converted again into an anhydride group by dehydration reaction during the bonding operation at high temperature. When HMAPE-EX's were used as adhesives [Fig. 3(c–f)], one can see that the peak height of the anhydride band at  $1784\text{ cm}^{-1}$  decreases and the peak height of ester band at  $1740\text{ cm}^{-1}$  increases as the amount of coated Epoxy-374 was increased. This indicated that an ester bond was formed by the reaction of carboxylic acid and epoxy groups by the second step of Reaction Scheme 1.

When one compares the bond strength and  $I_{1740}/I_{1784}$  (Table I), FTIR spectrum (Figures 1 and 3) of Se-



**Figure 2** FTIR spectra of the adhesives with the MAPE/Epoxy-374/MIZ compositions of (a) 100/4.2/0, (b) 100/4.2/0.03, (c) 100/4.2/0.06, and (d) 100/4.2/0.18.



**Figure 3** FTIR spectra of (a) MAPE, (b) HMAPE, and the adhesives with the HMAPE/Epoxy-374 compositions of (c) 100/0, (d) 100/1.8, (e) 100/4.2, and (f) 100/6.6.

rial number 1–8 with those of Serial number 14–19, it can be seen that the bond strength is higher and the evolution of the ester band at  $1740\text{ cm}^{-1}$  is more evident in Serial number 14–19 compared with those of Serial number 1–8, if the coated amount of Epoxy-374 is the same. As the  $n$  value of Epoxy-374 (see Chemical Structure 1) is as low as 0.12, the amount of hydroxyl groups is much lower than the amount of epoxy group. Consequently, the first step of Reaction Scheme 1 can be limited by the low concentration of reactive hydroxyl groups, when MAPE reacts with Epoxy-374. However, HMAPE can react with sufficient amount of epoxy groups of Epoxy-374 by the second step of Reaction Scheme 1. So, HMAPE can react faster than MAPE, and this enhanced reaction seems to be a cause of higher bond strengths of the Serial number 14–19 compared with those of Serial number 1–8.

## CONCLUSIONS

Our experimental results indicated that the bonding power of MAPE powder, which is used as a hot melt adhesive, could be improved substantially by coating a small amount of epoxy resin as a modifier. The FTIR spectrum showed that an ester bond was generated by the reaction between the anhydride groups of MAPE and the hydroxyl groups of epoxy resin during bonding operation, at  $190^\circ\text{C}$  with the pressure of 22 MPa for 30 min. A catalytic amount of MIZ accelerated the reaction, and consequently

elevated the bonding power. The enhancement of the reaction and the bond strength were also evident when the anhydride group of MAPE was converted to carboxylic acid groups by the reaction with water. This indicated that the acid groups, which can react with sufficient amount of epoxy groups, reacted faster with epoxy resin than the anhydride groups, which can react with limited amount of hydroxyl groups.

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