

Melt Grafting of Poly(ethylene-vinyl acetate) Copolymer with Maleic Anhydride

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ABSTRACT: Poly(ethylene-vinyl acetate) (EVA) copolymer was melt grafted with maleic anhydride (MAH) in a twin screw extruder in the presence of peroxide. It is confirmed that MAH has been melt grafted on the backbone of EVA by FTIR using the method of hydrolysis. The NMR analysis suggests that the grafting reaction occurs on the tertiary carbon of main chain of EVA other than the methyl moiety of vinyl acetate (VA) group. The incorporation of VA groups onto the matrix shows a competitive effect on the grafting. The existence of VA groups promotes the extent of MAH graft onto EVA; nevertheless, it also weakens the

crystallizability of main chain. When the content of peroxide initiator is 0.1 wt % based on the polymer matrix, the grafting degree increases with increasing the concentration of monomer. When the peroxide content is higher than 0.1 wt %, side reactions such as crosslinking or disproportionation will be introduced into this system. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 841–846, 2006

Key words: functionalization of polymers; graft copolymers; NMR; reactive extrusion; FTIR

INTRODUCTION

In recent years, much attention has been focused on grafting of maleic anhydride (MAH) onto polyolefins via reactive extrusion.^{1–3} The role of MAH functionalized polyolefin is to promote compatibilization between polar and apolar polymers,^{4,5} coupling between inorganic fillers and polyolefins^{6,7} as well as adhesion to metals.^{8,9} Maleated polyolefins have been rapidly developed for various and widespread applications.

Ethylene-vinyl acetate (EVA) copolymer, possessing both rubber and resin properties, is one of the important polyolefins and can be used as backbone of the graft copolymer. According to several studies,^{10,11} graft polymerization of MAH onto EVA copolymer in the melt in the presence of peroxide is usually accompanied by both crosslinking in the case of polyethylene and degradation in the case of polypropylene.

The maleation of EVA copolymers with a low amount of vinyl acetate (VA) (from 2.0 to 9.0 wt %) was studied by Gaylord et al.¹² Soares et al. studied the behavior of EVA copolymer with higher amounts of VA (18 and 28 wt %) toward the melt reaction with

MAH. It was found that the hydrogen abstraction in the EVA copolymer occurs both in the methyl group of the acetate moiety and in the tertiary C—H. The free radicals generated in the tertiary C—H react with MAH in a higher proportion.¹¹ Kim et al. found that the impact strength of PBT/EVA-g-MAH(80/20) blend showed about threefold increase in comparison with PBT/EVA(80/20) blend because of the enhanced interfacial adhesion by the formation of *in situ* compatibilizer.¹³ Kang et al. proved that PBT/EVA-g-MAH blends exhibit better impact strength than PBT/EVA, for the graft copolymer has larger interfacial adhesion with PBT than EVA.¹⁴ EVA-g-MAH as efficient compatibilizer to the PA6/EVA system was also reported by Bhattacharyya et al.¹⁵ and Liu et al.¹⁶ respectively.

Even though many works have been carried out by several research groups on the application of EVA-g-MAH, few papers have been reported on the reaction mechanism of MAH melt grafted onto EVA as a whole. The object of this study was to investigate some fundamental rules of the reaction of EVA copolymer melt grafting with MAH in a twin screw extruder in the presence of peroxide. FTIR and NMR were proposed for the quantification of grafted samples obtained from purification. The effects of VA group content and the concentrations of peroxide and MAH on the graft reaction were discussed, and the melt graft reaction mechanism was also studied.

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TABLE I
Typical Properties of Poly(ethylene vinyl acetate) Used in the Experiment

Brand	VA content (%)	Density (g/cm ³)	MFR (g/10 min)	Company
EVA14-2	13-15	—	1.70-2.40	Beijing organic chemical plant, China
EVATANE 2805	27-29	0.95	5-8	ATOFINA Chemicals, France
EVAFLEX 150	33	0.96	30	Mitsui Polychemical, Japan

EXPERIMENTAL

Materials

Poly(ethylene-vinyl acetate) (EVA) with different VA group content is used, and the typical properties are shown in Table I. Solvent (xylene, toluene, and acetone), MAH, DCP are all analytically pure and are used as received without any purification.

Preparation

Grafting is carried out in a twin screw extruder of 36 mm in diameter with $L/D = 38/1$. A premix blend of EVA pellets, MAH, and DCP in different proportion is fed into the extruder with a hopper at 200°C and 100 rpm. The extrudate is palletized and dried in vacuum oven at 60°C for 12 h.

Characterization

Purification

The purification process of grafting sample can be found in the literature.¹⁷ Sample (2-3 g) is dissolved in xylene at 130°C under reflux for 2 h, and then the temperature is lowered to 45°C and acetone is added. The precipitate is vacuum filtered and washed several times with acetone, followed by drying in vacuum oven at 60°C for 12 h.

Determination of grafting degree and gel content

Determination of reacted MAH is carried out based on the technique developed by Gaylord and Mishra.¹⁸⁻²⁰ Purified sample (0.3 g) is dissolved in 50 mL xylene saturated with water at boiling temperature, and a certain amount of DMF is added into the solution as an hydrolyzing agent. The hot solution is titrated with 0.02N ethanolic KOH using thymol blue as the indicator. Then, 1 mL excess of KOH solution is added and a deep blue color is back titrated to a yellow end point by the addition of 0.02N isopropanolic HCl to the hot solution. The grafting degree is expressed as the weight fraction of grafted MAH against polymer used in the reaction.

The gel content is analyzed with the method of soxhlet extraction. The grafted samples are put in Soxhlet for polymer matrix extraction with toluene for

8 h at boiling temperature. Then, the remnant is placed in vacuum conditions for weight constant. Gel content of graft samples is calculated with the weight loss in percent during extraction.

FTIR analysis

Infrared absorption spectroscopy performed in NEXUS 670 FTIR (NICOLET, American) is used to confirm the functionalization with pure EVA and purified grafted sample. Films for FTIR are compression molded at 140°C for 10 s, and then cooled to room temperature. The scan range is from 4000 to 400 cm⁻¹ at scan resolution of 4 cm⁻¹.

NMR analysis

Solid-state ¹³C NMR spectra are recorded with BRUKER AV 400 spectrometer at 400 MHz using cross polarization and magic angle spinning (CP/MAS) under room temperature. The zirconium oxide probe with diameter of 4 mm is encapsulated with Kel-F, and the solvent is acetone. 6 k of spinning rate, 1000 msec of contact time, and 3 s of delay time are used.

Hydrolysis of EVA and grafting sample

Two grams of pure EVA or purified grafting sample are dissolved in 100 mL xylene with the addition of ethanolic KOH, and refluxing for 2 h. The solution is then precipitated in cool acetone followed by vacuum filtered. The remnant is soxhlet extracted with acetone for 2 h and dried in vacuum oven at 60°C for 12 h to remove the residual solvent.

RESULTS AND DISCUSSION

FTIR spectroscopy

Infrared spectra corresponding to pure EVA and functionalized EVA are shown in Figure 1. Unfortunately, the presence of peaks at 1790 and 1865 cm⁻¹, characteristic of the carbonyl in the MAH, cannot be observed clearly because of the existence of acetoxy carbonyl carbon of the VA unit, which covers other bands in this zone. Only a few peaks in 1790 and 1865 cm⁻¹ are checked in the spectra of grafted EVA with com-

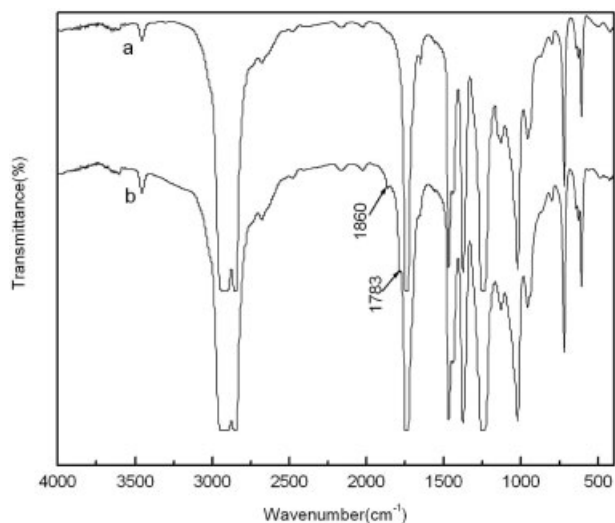


Figure 1 FTIR spectra of (a) EVA and (b) EVA-g-MAH.

parison to that of pure polymer, which might confirm the grafting reaction between EVA and MAH.

To weaken the influence of VA group on FTIR analysis, the method of hydrolysis is performed, which is also believed to be useful for determining the mechanism of grafting reaction in EVA,¹¹ and the schematic illustration of hydrolysis of EVA and its grafted product are described in Figure 2.

The hydrolysis products of EVA and EVA-g-MAH are expressed as EVAL and EVAL-g-MAH, respectively. The FTIR spectra are shown in Figure 3. Comparison with the spectra of EVA and EVA-g-MAH, the characteristic peak of carbonyl on VA group is sharpen and weaken but still exists, which is attributed to the strong absorption of carbonyl and also an indication of incomplete hydrolysis process in our experimental conditions. However, the existence of characteristic band near 1790 cm^{-1} corresponding to the carboxylic groups of MAH is confirmed, which

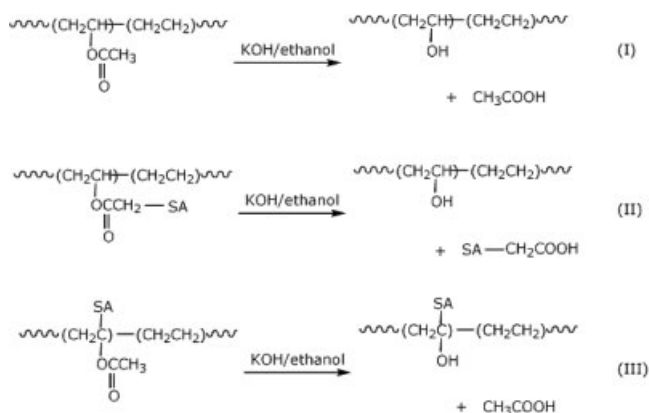


Figure 2 Schematic illustration of hydrolysis reaction of EVA and EVA-g-MAH SA: succinic anhydride.

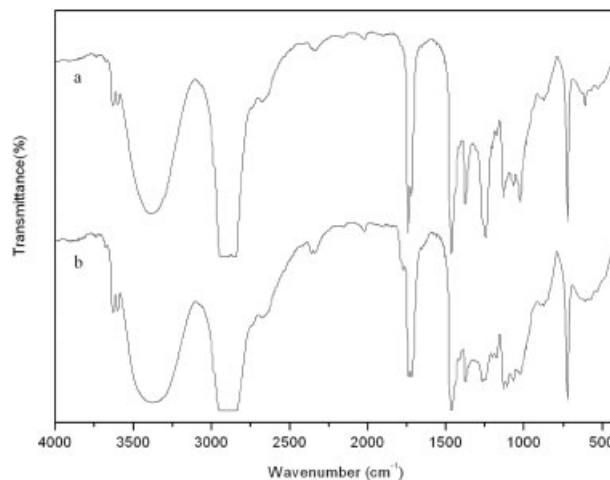


Figure 3 FTIR spectra of (a) EVAL and (b) EVAL-g-MAH.

should be regarded as the evidence of grafting reaction, since no similar band appears in the spectra of EVAL.

It is worthy noticing here that the FTIR analysis on hydrolysis product of EVA and its grafting samples prove the grafting reaction of MAH on the hydrogen atom of tertiary carbon at EVA main chain, otherwise, the peaks of MAH should disappear if the reaction takes place entirely in the hydrogen atoms of methyl units on VA groups. The discussion of grafting reaction mechanism on EVA with MAH will be revealed in next section with the assistance of NMR analysis.

NMR analysis

The existence of VA groups makes the grafting reaction more complicated with respect to that of polyethylene and polypropylene. The primary radical sites generated by peroxide initiator's decomposition are able to attack the hydrogen of tertiary carbon atom of polymer main chain and the carbon atom of methyl moiety in the VA group simultaneously, that is to say, the grafting of MAH onto EVA can perform in different mechanisms. Figure 4 illustrates different spectra of EVA with or without modification. The analysis on ^{13}C NMR spectra of EVA can be found in many literatures.^{22–24} Two signals of main chain of EVA were found in spectra of pure EVA: CH_2 from the ethylene rigid domain at 37.1 ppm and CH_2 from the ethylene flexible domain at 34.1 ppm; and three signals of VA group: carbon atom of $\text{CH}-\text{O}$ at 74.6 ppm, CH_3 attached to the VA group at 21.9 ppm, and $\text{C}=\text{O}$ at 174 ppm.

MAH is a symmetric molecule in structure, which means it can be characterized conveniently with NMR analysis. The electron density plot of MAH is shown in Figure 5,²⁵ and each carbon atom is labeled with C_5 to C_8 . The characteristic peaks of MAH in ^{13}C NMR

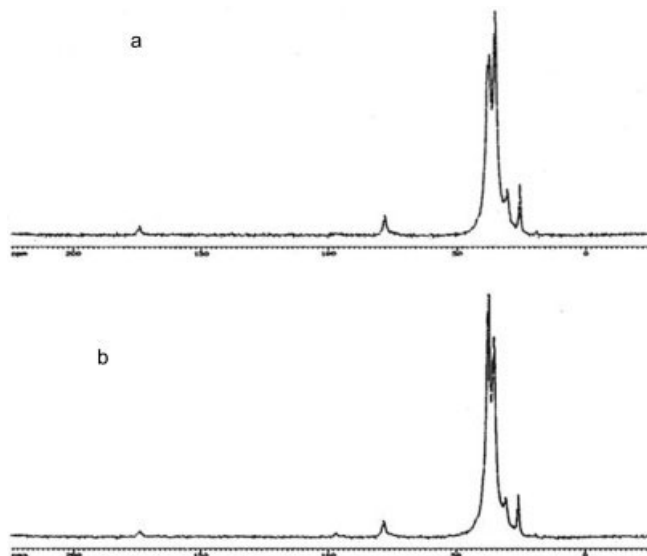


Figure 4 ^{13}C CP-MAS spectra of (a) EVA and (b) EVA-g-MAH.

analysis are $\text{C}_{5,6}$ at 45.1 ppm and $\text{C}_{7,8}$ at 174.1 ppm, respectively. No significant changes are found in chemical shift of the NMR spectrum of EVA-g-MAH [Fig. 4(b)] when compared with that of pure EVA. However, the intensity of signals at 37.1 and 34.1 ppm change strongly, which indicates the chemical reaction on main chain of EVA. On the other hand, the peak

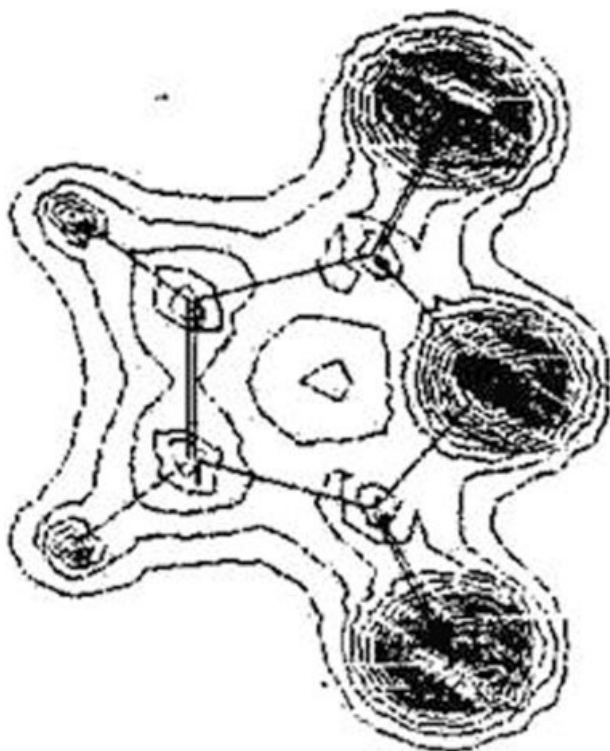


Figure 5 Electron density plot of MAH.

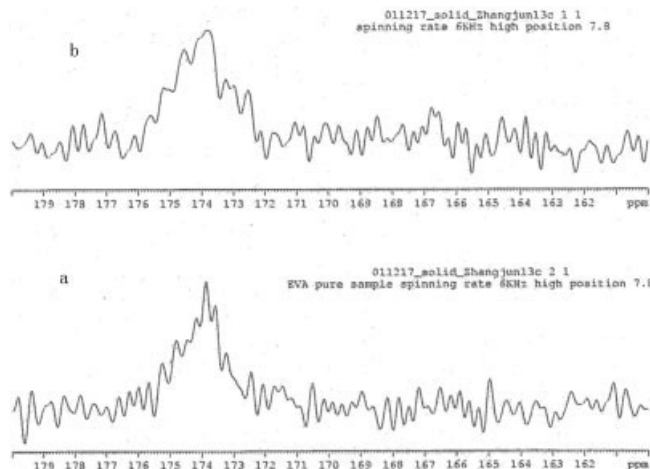


Figure 6 ^{13}C CP-MAS spectra of (a) EVA and (b) EVA-g-MAH from 162 to 180 ppm.

corresponding to the methyl moiety of VA group shows no changes in both intensity and chemical shift. Partial ^{13}C NMR spectra from 160 to 180 ppm were shown in Figure 6. New signals at 173 and 174.5 ppm due to the presence of carboxylic atoms of MAH confirm the functionalization of MAH onto EVA. The results suggest that the reaction occurs on the tertiary carbon of main chain other than the methyl moiety of VA group.

Influence of VA group on the grafting reaction

It is important to consider the influence of VA groups on the grafting reaction of EVA with MAH, so the grafting degree and efficiency of different polymer matrix are studied and the results are listed in Table II. Both the grafting degree and efficiency of EVA grafting with MAH are remarkably higher than those of PE or PP, which is due to the relatively stronger polarity of VA group of EVA when compared with methyl group of PP or hydrogen of PE. In fact, the melt grafting reaction is heterogeneous and the dispersion of monomer in matrix depends on the difference of the

TABLE II
Effect of the Nature of the Polymer Matrix on the Melt Functionalization

Polymer matrix	VA content (wt %)	Grafting degree (wt %)	Grafting efficiency (%)
LDPE	—	0.6672	22.24
PP	—	0.5818	19.39
EVA14-2	14	1.3209	44.03
EVA2805	28	1.5205	50.68
EVA150	33	0.7299	24.33

Polymer, 100 phr; MAH, 3 phr; DCP, 0.3 phr; Extrusion reaction conditions, 200°C and 100 rpm.

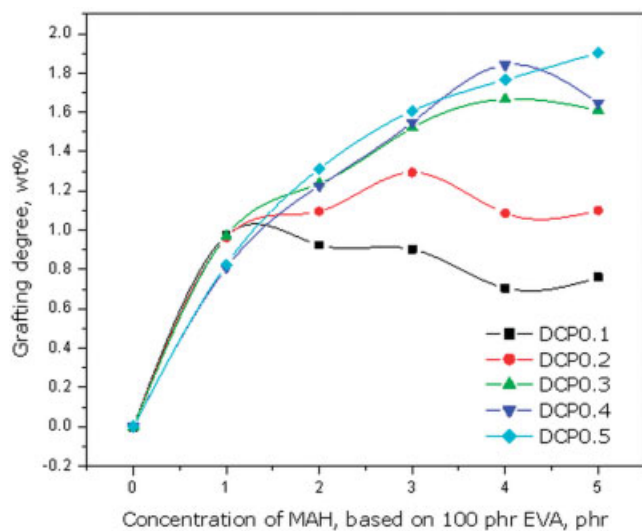


Figure 7 Effect of the concentrations of MAH and DCP on grafting degree of EVA-g-MAH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

viscosity and polarity between two components. Compared with PP or PE, the incorporation of VA group in the main chain eliminates the polar discrepancy of two components to some extent, so the degree of grafting reaction increases because of the improved compatibility.¹²

To study the effect of VA groups on graft reaction further, three types of EVA with different VA content are used. As presented in Table II, the grafting degree and efficiency of EVA with VA content at 28 wt % are higher than that of EVA with VA content at 14 wt %. The enhancement in polarity due to the increase in the amount of VA group promotes the extent of MAH graft onto EVA. However, in the case of EVA with VA content at 33 wt %, the decreases in the grafting degree and efficiency are observed. This might be attributed to the discrepancy in viscosity of the polymer matrix. The extent of the reaction increases only if this interface is continuously renewed by the action of shearing forces during the melt-mixing process.¹¹ While for the matrix with lower viscosity, the influence of shear forces on the renewed interface between polymer matrix and grafting monomer would be alleviated, resulting in a detrimental influence on the grafting reaction. Furthermore, as copolymer of two monomers, VA groups would debond from the main chain at about 200°C.²⁶ The existence of free VA groups could affect the decomposition manner of peroxide initiators because of its acidity, which hindered the grafting of monomer onto polymer because of the additional consumption of free radical sites.

Effect of the concentration of peroxide and MAH

The grafting reaction between polymer and monomer strongly depended on the concentration of peroxide

initiator and monomer, as shown in Figure 7. Generally, the grafting degree increases with the concentration of monomer and peroxide initiator increasing; however, it shows different phenomena in different cases.

When the content of peroxide initiator is quite low, for example, 0.1 wt % based on the polymer matrix, the macromolecular radical sites are formed because of the hydrogen deprivation by the primary radical sites caused by the decomposition of peroxide. First, the grafting degree increases with the content of MAH because of the increase in the reaction between monomer molecules and free radical sites. However, with the content of MAH increasing further, the separate phase of MAH will be formed because of the incompatibility between polymer and monomer. This is detrimental to the grafting reaction, since the mobility of monomer molecules is restrained. In addition, when the concentration of MAH reaches a certain level, the amount of peroxide initiator would be insufficient for the relatively higher concentration of MAH, leading to a decrease in the grafting degree. It must be pointed out here that no crosslinking reaction is checked in this system, which might be attributed to the inadequate concentration of peroxide.

Once the peroxide content reaches higher level, the excessive macromolecular radical sites affect the grafting reaction deeply, and the side reactions will be introduced into the system. Figure 8 is the dependence of gel content on the concentration of MAH at 0.5 wt % DCP based on polymer matrix. The gel content of system firstly decreases with the increasing amount of MAH. However, when the content of MAH reaches a certain level, it has little influence on the gel content. This reveals the competitive effect due to grafting and

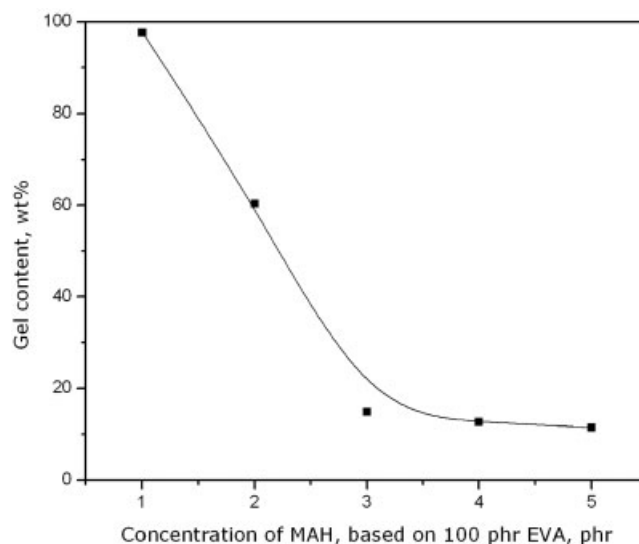


Figure 8 Effect of concentration of MAH on gel content, DCP = 0.5 phr.

crosslinking reaction in the system. Side reactions such as crosslinking or disproportionation consume considerable amount of macromolecular radical sites, which is detrimental to the grafting reaction. It is reported that EVA prefers to crosslinking under the existence of peroxides, and its crosslinking efficiency is higher than that of polyethylene.^{27,28} The predomination of grafting reaction at relatively higher concentration of monomer indicated the priority of grafting reaction against crosslinking reaction, which means the reaction between macromolecular radicals and monomer is obviously easier than the reaction between macromolecular radicals themselves. The work of Gaylord and coworkers suggest^{10,18-20,29} the existence of MAH excimers in the case of adequate amount of primary radical sites during grafting reaction process. The excimers are considered to be useful for the grafting of monomer with matrix because of the introducing of new activate sites caused by the interaction of stimulated monomer molecules.

CONCLUSIONS

The results discussed in this article indicate that MAH has been melt grafted on the backbone of EVA in a twin screw extruder in the presence of peroxide. The results of NMR suggested that the reaction occurs on the tertiary carbon of main chain other than the methyl moiety of VA group. The incorporation of VA groups onto the matrix promotes the extent of MAH graft onto EVA. However, the viscosity of polymer matrix has an important influence on the grafting reaction between polymer and monomer.

From the titration analysis of the grafted samples obtained from purification, it can be concluded that the graft reaction correlated with both the concentration of peroxide and that of MAH. When the content of peroxide initiator is 0.1 wt % based on the polymer matrix, the grafting degree increases with the concentration of monomer increasing. When the peroxide content is higher than 0.1 wt %, things will be more complicated. Side reactions such as crosslinking or disproportionation will be introduced into this system.

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