# Melt Functionalization of EVA Copolymers with Maleic Anhydride

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**ABSTRACT:** Ethylene vinyl acetate (EVA) copolymers with different amounts of vinyl acetate were melt-functionalized with maleic anhydride. The effect of benzoyl peroxide, *t*-butyl perbenzoate, and dicumyl peroxide (DCP) as free-radical initiators on the functionalization performance was studied. The crosslinking reactions occur to a larger extent than in polyethylene, indicating that the vinyl acetate groups favor the formation of free radicals. From all the experiments performed in this study, the recommended initiation system to achieve the best values of the functionalization degree and the lower gel content involves the use of DCP in a concentration of about 0.3 wt % and a maleic anhydride concentration around 5.0 wt %. From FTIR and TGA analyses, it is suggested that the hydrogen abstraction in the EVA copolymers 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 maleic anhydride in a higher proportion. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1799–1806, 1999

**Key words:** EVA copolymers; maleic anhydride; melt functionalization

## INTRODUCTION

Functional polymers carrying anhydride groups along the backbone exhibit enhanced adhesion properties to polar materials like polyamide, metals, and glass and are extensively employed as compatibilizing agents for polymer blends.[1,2] For technological and commercial purposes, the functionalization of polyolefins with maleic anhydride (MA) is better achieved in the melt process where the molten polymer is mixed with MA and an initiator in an extruder or mixing chamber at elevated temperature. This process is usually accompanied by crosslinking in the case of polyethylene,[3,4] degradation in the case of polypropylene,[5] and both phenomena with ethylene–propylene copolymers.[6]

The maleation of ethylene/vinyl acetate (EVA) copolymers was also studied by Gaylord et al.[7] As in the case of polyethylene, the authors also found a relatively high extension of crosslinked materials in reactions performed without the addition of stearamide. The mechanism proposed for the functionalization and crosslinking of EVA copolymers suggests radical reactions on the methyl groups of the acetate moiety. For those studies, EVA copolymers with a low amount of vinyl acetate (VA) (from 2.0 to 9.0 wt %) were employed.[7]

Considering that the presence of VA in the EVA copolymers exerts a strong influence on the polarity, processability, and reactivity of these copolymers, we decided to study the behavior of EVA copolymers with higher amounts of VA (18 and 28 wt %) toward the melt reaction with MA.

**Table I   Effect of the Nature of the Initiator on the Melt Functionalization of the EVA18 Copolymer or LDPE with MA**

| Polymer Matrix | Peroxide | Temperature (°C) | | MA Incorporation (wt %) | | Gel Content (wt %) | Final Torque (N m) |
|---|---|---|---|---|---|---|---|
| | | a | b | c | d | | |
| EVA18 | DCP | 110 | 120 | 0.3 | 6.0 | 3 | 8.4 |
| EVA18 | tBPB | 110 | 120 | 0.5 | 10.0 | 5 | 11.8 |
| EVA18 | BPO | 110 | 143 | 0.6 | 12.0 | 78 | 27.6 |
| EVA18 | DCP | 140 | 160 | 1.3 | 26.0 | 54 | 21.0 |
| EVA18 | tBPB | 140 | 164 | 1.2 | 24.0 | 70 | 25.4 |
| EVA18 | BPO | 140 | 164 | 1.3 | 26.0 | 80 | 26.4 |
| LDPE | DCP | 140 | 154 | 0.5 | 10.0 | 6 | 14.7 |
| LDPE | tBPB | 140 | 155 | 1.0 | 20.0 | 40 | 17.6 |
| LDPE | BPO | 140 | 155 | 2.0 | 40.0 | 54 | 20.6 |

MA: 5 wt %; peroxide: 0.5 wt %.
[a] Temperature employed in the experiment.
[b] Temperature reached at the end of the functionalization process.
[c] Amount of MA incorporated/100 g of polymer.
[d] Conversion of MA into succinic anhydride-grafted units in the copolymer, related to the initial amount of MA employed in the experiments.

This report deals with the influence of the chemical nature of the organic peroxide and other reaction parameters on the grafting efficiency and crosslinking during the melt functionalization of EVA copolymers.

## EXPERIMENTAL

EVA copolymers containing 18 wt % of VA (Petroquímica Triunfo S/A,Triunfo, Brazil) and 28 wt % of VA (Politeno S/A, Salvador, Brazil) were dried overnight at 50°C under a vacuum. MA was purified by distillation under a vacuum. Benzoyl peroxide (BP0), *t*-butyl perbenzoate (tBPB), and dicumyl peroxide (DCP) (Merck, Darmstadt, Germany analytical grade) were employed without purification.

The EVA copolymer was fluxed for about 2 min at 110 or 140°C in a Haake internal mixer at 60 rpm. Then, a mixture of MA and the organic peroxide was added at once and the reaction was kept under these conditions for 8 min.

The amount of insoluble material was determined by extracting about a 2-g sample of the crude copolymer in refluxing toluene for 24 h. The insoluble material was dried in a vacuum overnight at 60–80°C and weighted. The hot toluene layer containing the soluble functionalized EVA was poured into cold acetone to isolate the uncrosslinked material. The MA content of the soluble polymer was determined by titration of a hot-water-saturated toluene solution of the polymer with ethanolic KOH and thymol blue in DMF as an indicator, according to the literature.[7]

Thermogravimetric analyses were done on a TGA7 equipment under nitrogen and at a heating rate of $10°C.min^{-1}$. Infrared spectroscopy was done on a Perkin–Elmer 1720 FTIR. The spectra were recorded from films prepared by casting a toluene solution of the sample in a KBr disk.

## RESULTS AND DISCUSSION

### Studies on Melt Functionalization of EVA

The melt functionalization of EVA at two different temperatures was performed with three types of peroxide initiators and the results are shown in Table I. The data related to the functionalization of low-density polyethylene (LDPE) at 140°C are also presented. The MA incorporation into the EVA copolymer was relatively small for reactions carried out at 110°C. In spite of the low degree of functionalization, the gel content for reactions

initiated by BPO was very high. According to the literature,[7] the primary free radicals generated from the peroxide decomposition abstract hydrogen atoms from the acetate moiety in the EVA backbone. The active sites on the polymer give rise to MA grafting reactions and crosslinking. Therefore, the results observed in Table I indicate that the primary radicals from BPO have a higher ability in abstracting the hydrogen from the polymer backbone. The formed free radicals react preferentially with other polymer chains, giving rise to crosslinking reactions rather than to a graft reaction, probably because at 110°C the dispersion of the MA particles is not enough to be reached by a great amount of these free radicals.

Increasing the temperature increases also the MA content in the EVA copolymer but these values were not influenced by the chemical structure of the initiator. It is important to point out that the crosslinking degree is higher in EVA copolymers than in LDPE, indicating the influence of the VA groups in this process.

The functionalization process promotes an increase in the melting temperature, but no relationship was found between this phenomenon and the MA incorporation or crosslinking degree for reactions performed at 140°C. At 110°C, the melt functionalization in the presence of BPO takes place with a significant increase in the reaction temperature and final torque, which is in agreement with the results concerning the gel content.

The rheological behavior during the melt functionalization can be observed from the torque profiles. Figure 1 illustrates the torque developed during the reaction of EVA18 at 140°C. The reaction carried out with DCP is characterized by a continuous increasing of the torque with the time, whereas those initiated by tBPB or BPO involve a sudden increase in torque at the beginning of the process.

For the systematic studies on the functionalization of EVA, DCP was employed as a free-radical generator because of the lower degree of crosslinking achieved with this peroxide. The effect of the copolymer composition on the grafting efficiency is summarized in Table II. In all the systems studied, the amount of insoluble material increases with the MA concentration. This behavior was also reported in the literature during the functionalization of HDPE and attributed to the formation of more polymer radicals due to the presence of the excited MA.[4]



**Figure 1** Torque profiles obtained during the melt functionalization of EVA18 at 140°C, using different types of peroxide initiators.

Concerning the graft efficiency, both EVA18 and EVA28 displayed higher degrees of MA incorporation than did LDPE. The grafting reaction was more effective with the EVA18 copolymer. Since the presence of VA groups in the EVA copolymers may facilitate free-radical reactions, a higher MA incorporation would be expected for the EVA28 sample because of the greater amount of these groups. The peculiar behavior found in our system may be attributed to the difference in the viscosity of the medium associated with the incompatibility of the polymer matrix and the functionalizing agent, MA. In spite of the presence of VA groups, the EVA copolymers cannot be considered as polar materials. Therefore, the polar MA molecules are not miscible in the EVA matrix and tend to form a separated phase. As discussed in the literature,[8] the reaction in such systems takes place only at the interface. Thus, the extent of the reaction increases only if this interface is continuously renewed by the action of shearing forces during the melt-mixing process. As illustrated in Figure 2, the torque developed during the functionalization of EVA28 is significantly lower than that observed with EVA18 for the same reaction conditions. This means that EVA28 functionalization takes place under lower shearing forces. In these mixing conditions, the dispersion of MA into the EVA28 matrix may not be as effective, resulting in a lower grafting efficiency.

**Table II  Grafting Efficiency and Gel Content as a Function of the Copolymer Composition**

| Polymer Matrix | VA Content in the Matrix (wt %) | MA Concentration (wt %) | Temperature (°C) | MA Incorporated (wt %) | | Gel Content (wt %) |
|---|---|---|---|---|---|---|
| | | | | a | b | |
| EVA18 | 18 | 5 | 110 | 0.3 | 6 | 3 |
| EVA18 | 18 | 10 | 110 | 0.4 | 4 | 4 |
| EVA28 | 28 | 5 | 110 | 0.3 | 6 | 3 |
| EVA28 | 28 | 10 | 110 | 0.8 | 8 | 8 |
| LDPE | 0 | 5 | 140 | 0.6 | 12 | 6 |
| LDPE | 0 | 10 | 140 | 0.6 | 6 | 9 |
| EVA18 | 18 | 5 | 140 | 1.3 | 26 | 54 |
| EVA18 | 18 | 10 | 140 | 2.1 | 21 | 60 |
| EVA28 | 28 | 5 | 140 | 0.9 | 18 | 10 |
| EVA28 | 28 | 10 | 140 | 1.0 | 10 | 16 |

DCP: 0.5 wt %.
[a] Amount of MA incorporated/100 g of polymer.
[b] Conversion of MA into succinic anhydride-grafted units in the copolymer, related to the initial amount of MA employed in the experiments.

The effect of MA concentration on the functionalization of EVA18 is illustrated in Figure 3. As indicated in Figure 3(a), the amount of MA incorporated into the copolymer increases with the initial MA concentration until about 5 wt % for reactions performed with 0.2 wt % of DCP. At a



**Figure 2**  Torque profiles obtained during the melt functionalization of EVA18 and EVA28. Temperature = 140°C; time = 10 min; MA = 5 wt %; DCP = 0.5 wt %.

higher peroxide concentration, the amount of MA is lower but increases continuously until 10 wt % of MA. However, if one takes into account the conversion of MA into appendage succinic anhydride units in the copolymer backbone (reaction extent), these values decrease substantially [see Fig. 3(b)]. This behavior is also an indication of the incompatibility of both components (EVA18 and MA). The MA molecules tend to form aggregates dispersed into the EVA matrix. Increasing the amount of the MA component also increases the proportion of MA located inside the phase and, consequently, inaccessible to the free-radical sites in the polymer matrix.

Reactions performed with 0.2 wt % of DCP resulted in a crosslinking degree of 7–10% whatever was the amount of MA employed. For reactions performed with 0.5 wt % of DCP, the amount of insoluble material increased to 55–60% without increasing the functionalization performance. The effect of the DCP concentration on the MA content incorporated into the EVA18 matrix and on the gel content is better illustrated in Figure 4(a,b), respectively. The amount of MA content increased with the DCP concentration when the amount of this component was relatively low. When a DCP concentration as high as 0.5 wt % was employed, decreasing the MA con-

**Figure 3** Effect of MA concentration on the (A) amount of MA incorporated into the copolymer and (B) conversion of MA into appendage succinic anhydride units during the melt functionalization of EVA18.

tent resulted in an increase in the amount of insoluble material observed.

### Fourier Transform Infrared Spectroscopy and TGA Analysis

The grafting reactions in EVA copolymers may take place on the methyl group of the acetate moiety or on the tertiary C—H. These possibilities are illustrated in Figure 5. According to the results discussed above and considering the mechanism proposed in the literature,[7] it is believed that these reactions occur preferentially on the methyl group [eq. (I)]. To confirm this behavior, a soluble fraction of functionalized EVA (EVA–MA containing 2.1 wt % of MA) was submitted to hydrolysis with a methanolic solution of NaOH. The same procedure was

also employed with the EVA18 sample. If the grafting reaction occurs preferentially in the acetate moiety, the hydrolyzed product of EVA–MA should yield similar characteristics as those of the hydrolyzed EVA (namely, EVAL). On the other hand, if the site of hydrogen abstraction is at the tertiary C—H, the hydrolyzed product of EVA–MA will keep the succinic anhydride moiety even after the hydrolysis. The possible hydrolyzed products are illustrated in Figure 6.

To compare the structural features of EVA and EVA–MA and the corresponding hydrolyzed products, FTIR and TGA analyses were employed. Figure 7 displays the FTIR analysis of these samples. The spectra of the EVA and EVA–MA present a typical absorption at 1739 cm$^{-1}$ related



**Figure 4** Effect of the DCP concentration on the (A) amount of MA incorporated into the EVA18 copolymer and (B) gel content.

**Figure 5**  Possibilities for the melt functionalization of the EVA copolymer.

to carbonyl of the ester and/or anhydride groups. Both spectra are similar. The absorption of the carbonyl group concerning the anhydride groups in EVA–MA cannot be distinguished because of the high amount of ester groups in this sample. The hydrolysis of EVA gave rise to a product free of ester groups, as indicated by the absence of the absorption at 1739 cm$^{-1}$ in the spectrum of EVAL. However, the spectrum of the hydrolyzed EVA–MA (EVAL–MA) displayed a small absorption related to the carbonyl groups, indicating that grafting reactions may also be occurring in the tertiary C—H, as illustrated in eq. (V) of Figure 6.

To quantify the succinic anhydride appendage remaining in the EVA copolymer after the hydrolysis, we submitted the EVAL–MA to titration. An amount of 1.9 wt % of anhydride groups was obtained. Since the EVA–MA sample used in this experiment contained 2.1 wt % of this group, we can conclude that the most anhydride groups present in the EVA–MA were incorporated through the free radicals formed in the tertiary C—H of the EVA backbone [eq. (II)].

The insoluble material of the EVA–MA sample was also submitted to hydrolysis. After this treatment, around 30% of the material still remained insoluble as a consequence of the crosslinking of the tertiary C—H. The other 70% is related to the hydrolysis of the acetate moiety and crosslinking on the methyl group of the acetate moiety.

The TGA thermograms of EVA, EVA–MA, and the corresponding hydrolyzed products (EVAL and EVAL–MA) are shown in Figure 8. The thermal degradation behavior of EVA and EVA–MA are quite similar [Fig. 8(A)]. The TGA curves of the hydrolyzed products [Fig. 8(B)] present different profiles. The decomposition of EVAL–MA started at a lower temperature than did that of EVAL. This behavior is viewed also as an indication of the presence of anhydride groups in the hydrolyzed product which seem to degrade at the beginning of the process.

## CONCLUSIONS

The results discussed in this report indicate that the functionalization of EVA copolymers is more effective than that of LDPE for reactions performed at 140ºC and initiated by DCP. The amount of insoluble material is higher in functionalized products of EVA18, indicating that the VA groups in the EVA copolymer are involved in this phenomenon. In spite of the higher VA content in the EVA28 copolymer, the functionalization efficiency is lower than with EVA18, probably because of the lower viscosity developed during the EVA28 reaction process. The lower viscosity does not help disperse the MA agglomerates. Since both MA and EVA copolymers are incompatible, a high amount of MA molecules located inside the MA domains are inaccessible to the functionalization system. This also explains



**Figure 6**  Chemical structure of the hydrolyzed products from the melt functionalization of EVA with MA.

**Figure 7** FTIR spectra of EVA, EVA–MA, and their hydrolyzed products.

the decrease in the MA conversion into a succinic anhydride appendage with increasing amounts of MA added to the reaction medium.

From the FTIR results and the titration analysis of the hydrolyzed product of EVA–MA, we can conclude that the grafting reaction of MA into the EVA copolymer occurs predominantly on the tertiary C—H of the backbone, contrarily to the mechanism proposed by Gaylord et al.[7] On the other hand, the crosslinking reactions occur on



**Figure 8** Thermogravimetric curves of (A) EVA and EVA–MA and (B) their hydrolyzed products.

both methyl groups of the acetate moiety and tertiary C—H sites, as indicated by the amount of insoluble and soluble materials which still remained after hydrolysis of the insoluble part of the reaction medium (around 30 and 70 wt %, respectively). All the results obtained in this work indicate that the formation of free radicals in the EVA copolymer occurs at both sites but the tendency is for the grafting reaction to take place mainly in the tertiary C—H. This behavior is intriguing but interesting. According to the TGA of EVA and EVA–MA, the acetate groups are the first to be decomposed. Therefore, the anhydride groups in the EVA–MA copolymers should not be affected by the high temperature normally used in the processing of the blends because they are not joined at the acetate moiety. Since these EVA-functionalized copolymers are supposed to be used as compatibilizer agents, this behavior may be useful.

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