

# Structure and Properties of Blends of Poly(ethylene-*co*-vinyl alcohol) with Poly(styrene-*co*-maleic anhydride)

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**ABSTRACT:** In the present study, ethylene/vinyl alcohol (EVAL) copolymers with different hydroxyl contents were melt mixed with styrene/maleic anhydride (SMA) copolymers. These two copolymers have functional groups capable of reacting intermolecularly, giving stable products. All EVAL copolymers were prepared from the same ethylene/vinyl acetate (EVA) copolymer by controlled hydrolysis. The blends, prepared at constant temperature and rotation speed in the rheomixer, were characterized by Fourier transform infrared spectroscopy, differential scanning calorimetry, and thermogravimetric analysis, as well as mechanical properties and extraction experiments. All the above measurements lead to the conclusion that a certain part of hydroxyls of EVAL have reacted with anhydride groups of SMA, leading to the formation of branched and crosslinked products. The effect of (1) the molar ratio of hydroxyl/maleic anhydride functional groups, (2) the overall concentration of the functional groups, and (3) the mixing time on the structure and properties of the blends are discussed. Emphasis is given on the influence of these factors on the tensile strength, the elongation at break, and impact strength of the products. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 983–999, 1997

**Key words:** reactive blending; polymer blends; compatibilization; ethylene-*co*-vinyl alcohol; styrene-*co*-maleic anhydride

## INTRODUCTION

A substantial part of the synthetic polymers ends up, after a short usage time (usually in a form of packaging material), in the environment as litter. However, the long time required for their degradation results in a significant accumulation of plastic litter in the environment. Legislative restrictions imposed on the use of plastics for environmental protection purposes have often made the introduction of new monomers and

polymers into industrial scale production a rather time-consuming and expensive process.<sup>1</sup> Also, since monomers are usually produced from nonrenewable energy sources like oil, plastics disposal results in a significant waste of energy, and raw materials. As a result, in the last few years, a significant part of research on polymeric materials is directed towards polymer recycling. Plastics to be recycled are not always pure polymers, and their separation is not trivial. Thus, recycling often means blending of different, already used polymers. Although there are many miscible polymer pairs known, in general, most pairs are immiscible. Miscibility is not a *sine qua non* condition for producing useful polymer blends. In many cases, however, the high degree

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of immiscibility of most polymers is a significant problem in the usage of polymer blends as it results in the production of blends with inferior mechanical properties.<sup>2</sup>

Polyethylene (PE) and polystyrene (PS) are two of the most widely used polymers for a variety of applications. Annual worldwide production of polyethylene is 39.2 billion pounds and of polystyrene 9.7 billion pounds.<sup>3</sup> Thus, there is, much interest in recycling them. Mixing of these two polymers in order to reuse them leads to blends with inferior mechanical properties due to their immiscibility at all proportions.<sup>4-6</sup> To overcome this problem and to improve the mechanical properties of PE/PS blends, block or graft copolymers have been used as compatibilizers.<sup>4,7-15</sup> Compatibilizers act in a manner similar to emulsifiers, reducing the interfacial energy of phases and reducing their size. Usage of triallyl isocyanurate (TAIC) as coupling agent in PE/PS blends in the presence of dicumyl peroxide and styrene monomer has led to a reduction of interfacial tension and improved properties through the formation of PE-TAIC-PS poly-alloy.<sup>16-19</sup> Direct grafting of PS on PE can also be achieved using ethylene/vinyl alcohol copolymer modified by mercaptoacetic acid and styrene monomer.<sup>20</sup> Partial compatibilization can also be achieved using functionalized PE and PS containing groups capable of reacting *in situ*, leading to grafting or crosslinking of the two polymers.<sup>21-24</sup> The produced copolymers can act as compatibilizers.

This last technique has gained significant interest in the last few years due to the advantages it has, mainly, its lower cost. Compatibilization can be achieved during the processing of polymers, e.g., in a twin screw extruder without any need for prior compatibilizer preparation via chemical synthesis.

In this study, the polymers used were styrene/maleic anhydride (SMA) copolymers and ethylene/vinyl alcohol (EVAL) copolymers. These two copolymers have functional groups capable of reacting intermolecularly, giving stable products. The present article contains the first part of the study undertaken, and it deals with the reaction of the functional groups; the structure of the products formed; and their thermal, morphological, and mechanical properties. All these properties depend on many factors related to both the nature of the mixed copolymers as well as the mixing conditions. In this work, we have tried to keep as

many of these factors as possible constant and to systematically change a few.

## EXPERIMENTAL

### Materials

In this study, two copolymers of polystyrene modified with maleic anhydride (SMA) were used, supplied by Arco Chemicals. The two random SMA copolymers, Dylark 232 with  $\bar{M}_w = 200,000$  and Dylark 332 with  $\bar{M}_w = 180,000$ , contained 8.4 mol% (SMA8) and 14.7 mol% (SMA14), respectively. EVAL copolymers with different hydroxylic contents, namely 1.6 (EVAL16), 3.2 (EVAL32), 6.5 (EVAL65), and 7.5 mol% (EVAL75) were obtained by hydrolysis of an ethylene-vinyl acetate (EVA) copolymer containing 8 mol% (EVA8) vinyl acetate (Alcudia). The hydrolysis was made in toluene solution using a methanolic solution of sodium hydroxide.<sup>20</sup> Extent of hydrolysis was controlled by varying the reaction time and was followed by Fourier transform infrared (FTIR) spectroscopy.

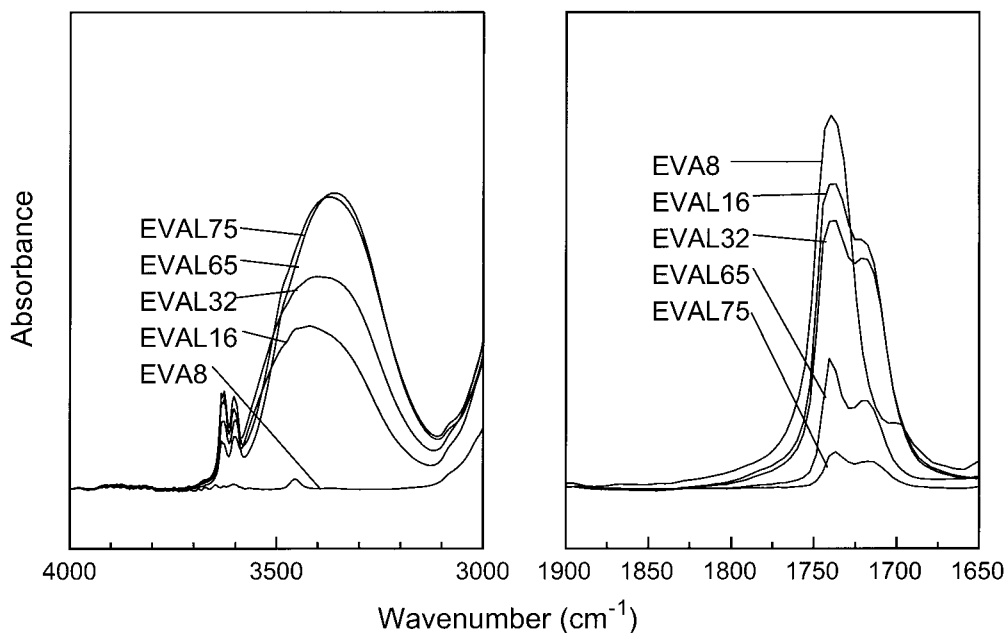
### Procedures

All the reactive blends were melt blended in a Haake-Buchler Rheomixer, Model 600, with roller blades. The coupling reaction of SMA8 with the polyethylene/vinyl alcohol copolymers, was carried out at 200°C and 60 rpm for a period of 20 and 30 min. The coupling of SMA14 with the four polyethylene/vinyl alcohol copolymers was carried out at the same conditions for 30 min. SMA blends with nonhydrolyzed polyethylene/vinyl acetate copolymer were also prepared, to be used as reference materials. All blends contained equal weights of SMA and EVAL, leading to a 50 : 50 by weight composition. The two polymers were physically premixed before being fed to the Rheomixer. The melt temperature and torque were continuously recorded during the mixing period on a Haake Rheocord, Model 5000. After the mixing period, the blends were immediately removed from the mixer, cooled to room temperature, and ground to small pieces.

### Characterization

#### FTIR

Compression-molded films about 70  $\mu\text{m}$  thick were used. FTIR spectra were recorded on a Bi-



**Figure 1** FTIR spectra of EVA and its hydrolyzed derivatives for two spectral regions: hydroxyls (left); carbonyls (right).

rad spectrometer (Model FTS-45A) at a resolution of  $2\text{ cm}^{-1}$  using 64 coadded scans.

#### Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) thermograms were recorded using a Shimadzu differential scanning calorimeter (model DSC-50Q), using indium as a calibration standard. About 6 mg from each sample were used with the exact weight measured in a precision balance. Samples were initially heated under a nitrogen atmosphere up to  $200^{\circ}\text{C}$  with a heating rate of  $20^{\circ}\text{C}/\text{min}$  to erase all previous thermal history; subsequently, they were immediately quenched. The sample was rescanned under the same conditions and from this second recording,  $T_g$ ,  $T_m$ , and  $\Delta H_m$  were determined.  $T_g$  was defined as the midpoint of the transition peak.  $T_m$  and  $\Delta H_m$  were defined as the peak maximum and the area of the melting peak, respectively.

#### Thermogravimetric Analysis

Thermogravimetric analysis (TGA) measurements were performed on a Shimadzu thermogravimetric analyzer (Model TGA-50). Samples were heated under a nitrogen atmosphere at a heating rate of  $20^{\circ}\text{C}/\text{min}$  and a final temperature of  $650^{\circ}\text{C}$ . The initial sample weight was about 8 mg.

#### Extraction Experiments

For the extraction experiments on our samples, thin films, approximately  $70 \pm 5\ \mu\text{m}$  thick, were prepared by compression molding in an hydraulic press. These films were extracted first in boiling acetone to remove unreacted SMA. The extraction was continued until constant weight was attained (about 12 h). The insoluble part was then extracted with boiling toluene. The hot toluene solutions were immediately filtered through pre-weighed Gooch filters. The polymer was isolated from the filtrate by addition of methanol and fil-

**Table I** Table of —OH/—COOCO— Molar Ratios for EVAL/SMA Blends Prepared

Blend	Composition (wt %)	—OH/—COOCO— Molar Ratio
EVAL16/SMA8	50 : 50	0.20
EVAL32/SMA8	50 : 50	0.40
EVAL65/SMA8	50 : 50	0.77
EVAL75/SMA8	50 : 50	0.90
EVAL16/SMA14	50 : 50	0.10
EVAL32/SMA14	50 : 50	0.20
EVAL65/SMA14	50 : 50	0.44
EVAL75/SMA14	50 : 50	0.51

tration of the precipitated polymer. The insoluble, possibly crosslinked fraction retained on the Gooch filter was washed first with hot toluene and then with methanol. The filters were subsequently dried to constant weight, and the insoluble fraction was determined from the difference of filter weights after and before filtration. The various polymer fractions obtained through this process were subsequently characterized.

### Mechanical Properties

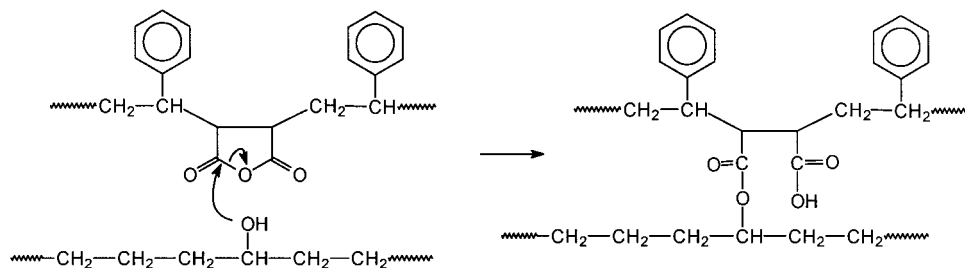
Tensile strength tests were performed on an Instron mechanical analyzer (Model 1122) with a crosshead rate of 0.5 cm/min according to ASTM D638. Izod impact tests were performed on a Tinius Olsen instrument according to ASTM D256.

## RESULTS AND DISCUSSION

### Blending

Figure 1 depicts the FTIR spectra of EVAL samples used for the blends preparation together with the spectrum of the nonhydrolyzed polyethylene/vinyl acetate copolymer.

The different intensity of the broad peak in the region between 3600–3100  $\text{cm}^{-1}$  is due to the different hydroxyl content of the samples. The increase of the hydroxyl peak in the samples is followed by a concurrent decrease in the carbonyl peak centered



By controlling the proportions of the reacting functional groups, it is possible to adjust both the extent of reaction and the structure of the crosslinked material. This is important since extensive crosslinking can lead to an undesirable increase in the melt viscosity of the product and, at the end, to an undesirable product. At the extremes of the composition range of the blend, an extensive reaction can also render one of the constituent polymers (the minor component

at around 1740  $\text{cm}^{-1}$ , which is attributed to the ester carbonyl groups of vinyl acetate.

Using the area of this peak as a measure of vinyl acetate content, it was possible to determine the hydrolyzed fraction of vinyl acetate groups. To do this, the area of the peak at 1740  $\text{cm}^{-1}$  for each EVAL sample was first divided by the absorbance at 1470  $\text{cm}^{-1}$  ( $\delta_{(\text{CH}_2)}$ ), which was used as an internal thickness band (a band that depends only on the quantity of sample). This procedure gave carbonyl peak areas that were corrected for thickness differences among the samples. The hydrolyzed fraction  $H$  for each sample was then calculated as  $H = A_{\text{corr}}/AO_{\text{corr}}$ , where  $A_{\text{corr}}$  is the corrected carbonyl peak area of the sample, and  $AO_{\text{corr}}$  is the respective area of the unhydrolyzed (EVA8) polymer.

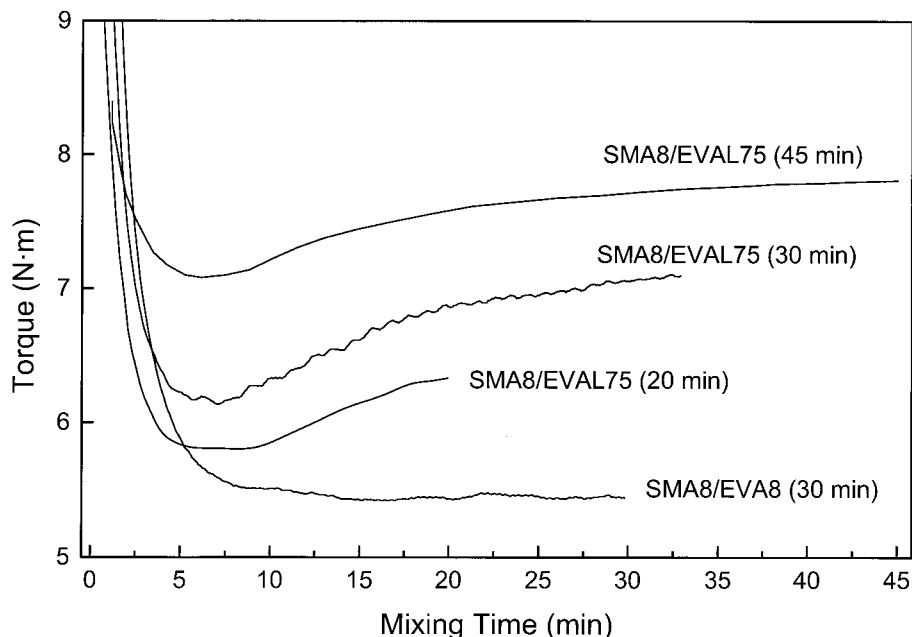
Since the EVA8 copolymer contained 8 mol% vinyl acetate, it was possible to calculate the percentage of hydroxyl content by a simple multiplication of the corresponding hydrolyzed fraction by eight for each sample prepared.

By using samples hydrolyzed to a different extent, we were able to prepare SMA/EVAL blends with different proportions of maleic anhydride/hydroxyl groups. The blends prepared and their respective hydroxyl/anhydride molar ratios are shown in Table I.

As a consequence, the blends prepared are expected to have different content of crosslinks created during the reaction of hydroxyl groups with maleic anhydride units as shown below.

with many reacting groups) totally inaccessible; as a result, the product may lose its compatibilizing properties.<sup>25</sup>

Prior to preparation of the samples, it was decided to study the effect that the mixing time has upon the product properties. Thus, SMA8/EVAL75 mixtures were prepared using three different mixing times, namely, 20, 30, and 45 min. Mixing of the polymers was performed at a temperature of 200°C and a rotation speed of 60 rpm.



**Figure 2** Torque versus time diagram of SMA8/EVAL75 and SMA8/EVA8 mixtures for different mixing times.

The torque diagrams for these samples are presented in Figure 2, together with that of the SMA8/EVA mixture.

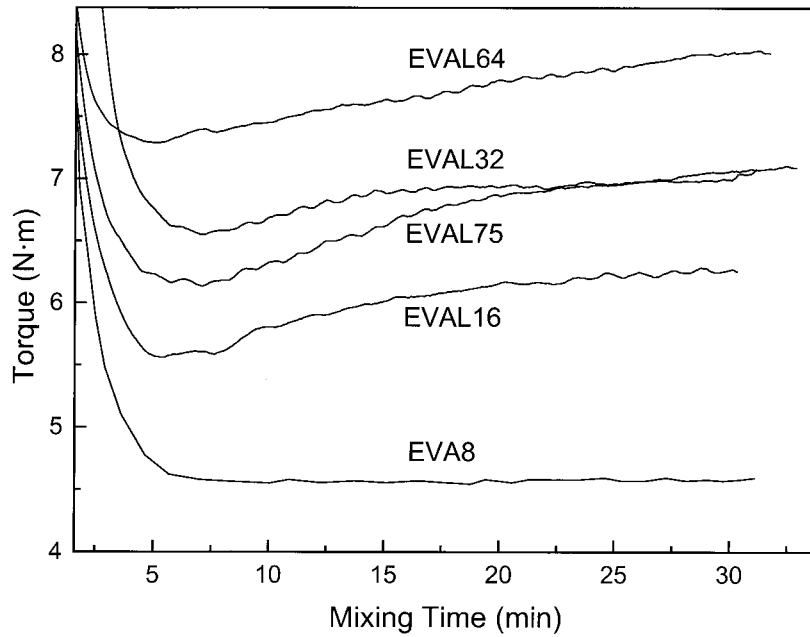
For the SMA8/EVA mixture, the torque remains constant after the melting of polymers throughout the mixing period. This is an indication that no significant degradation or reaction between the two polymers is occurring within this time period. This was also confirmed by FTIR analysis of the resulting mixture.

In contrast, for the SMA8/EVAL75 mixture, there is an increase in torque immediately after the initial melting of the polymers. This is due to the reaction between the functional groups of the two polymers, which leads to the formation of branched and crosslinked molecules, which now have higher melt viscosity. In the SMA/EVA system, this reaction is, of course, impossible since there are no functional groups capable of reacting.

From the torque monitoring, we can follow both the onset and the progress of the reaction, as well as its completion. From the study of the torque diagrams, it is concluded that the reaction starts within 5–6 min of mixing time and is completed after approximately 45 min. Such long mixing times are undesirable for industrial processing conditions in equipment such as twin screw extruders, where usually the residence times vary

from a few seconds up to at most 20 min.<sup>26</sup> Such a long reaction time may also lead to the formation of a highly crosslinked product due to extensive reaction between the reactive groups of the polymers. As a consequence, it was decided to use two mixing times for the SMA8 mixtures, namely, 20 and 30 min. This was done in order to study the extent of reaction versus the reaction time. For SMA14 mixtures, the mixing time was set to 30 min. The torque variation of SMA8 mixtures for 30 min mixing time are presented in Figure 3.

Mixtures with EVAL16 and EVAL32, which have the lowest hydroxyl levels, show the smallest increase in torque. In addition, the torque in these mixtures is stabilized within the 30 min mixing period, indicating possible completion of the reaction. The most probable explanation is that all the hydroxyls have reacted since there is a great excess of anhydride groups. Another possible explanation is that only a fraction of reactive groups are accessible for reaction. Similar observations can be made for SMA14/EVAL mixtures, as seen in Figure 4. The only difference is observed in the torque increase, which is more pronounced and slightly larger in SMA14 mixtures compared to the SMA8/EVAL mixtures. This may be due to a higher reaction speed as a consequence of the increased concentration of anhydride groups.



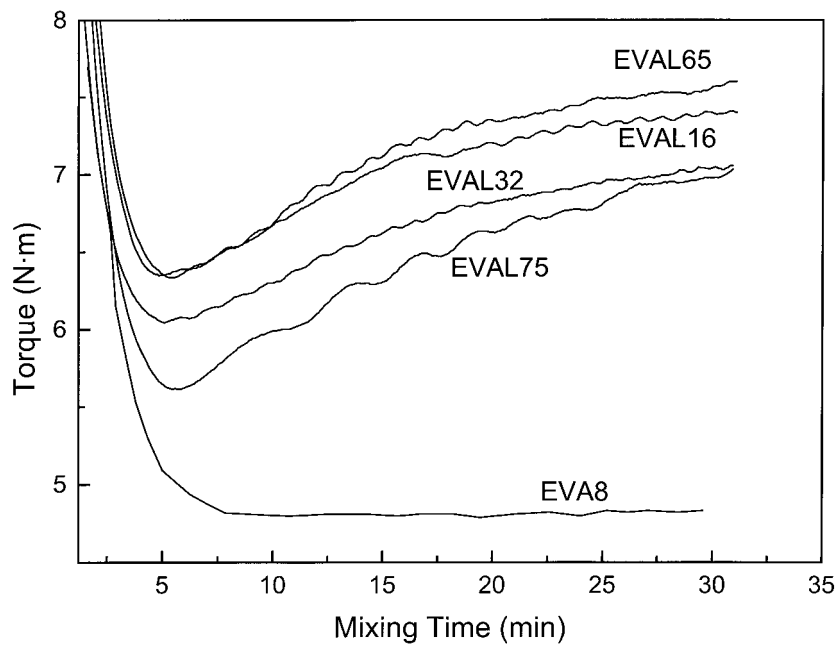
**Figure 3** Torque diagrams for SMA8/EVAL blends (30 min mixing time).

**FTIR Study**

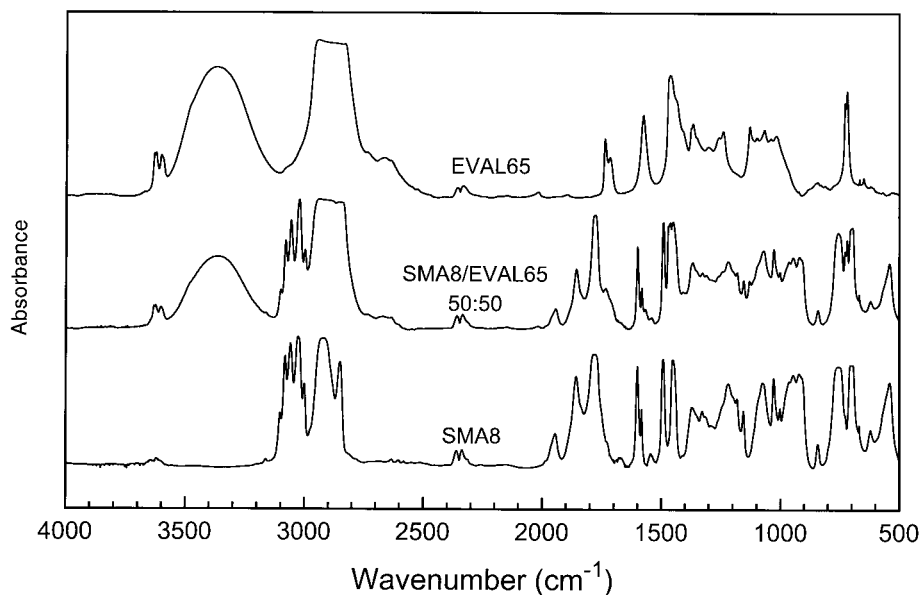
The prepared polymer blends were studied using FTIR spectroscopy. Figure 5 shows the spectra of

the product of SMA8/EVAL65 melt mixing and of the corresponding pure polymers.

In the SMA8 spectrum, there are two characteristic peaks at 1858 and 1780  $\text{cm}^{-1}$ , which are



**Figure 4** Torque diagrams for SMA14/EVAL blends (30 min mixing time).

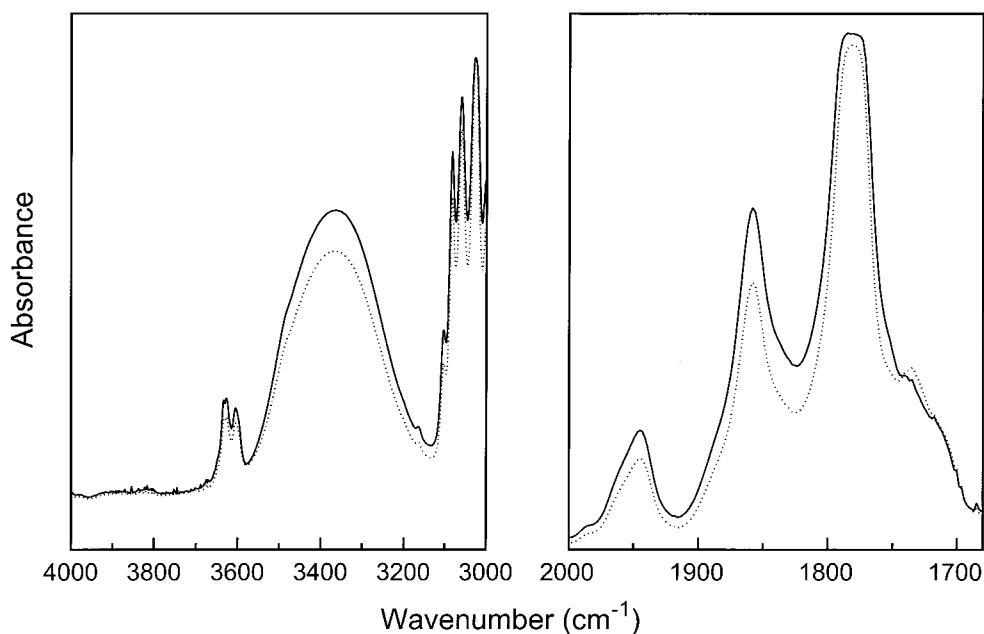


**Figure 5** FTIR spectra of SMA8, EVAL65, and their blend after 30 min of mixing.

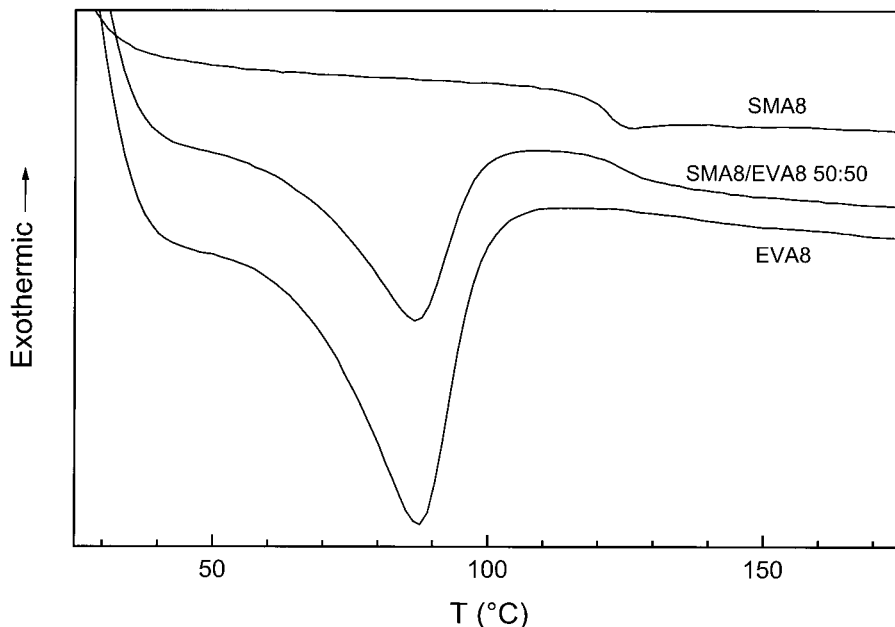
attributed to the saturated five-membered anhydride ring<sup>27</sup> and to the symmetric and antisymmetric stretching vibration of the maleic anhydride groups, respectively. The characteristic peaks of styrene at 1620 and 3100–3200  $\text{cm}^{-1}$  can also be observed in the figure. In the EVAL spectra, one can observe the hydroxyl peak at 3100–

3600  $\text{cm}^{-1}$  and polyethylene peaks at 1460 and 730  $\text{cm}^{-1}$ . There is also a weak absorption at 1740  $\text{cm}^{-1}$  due to the carbonyl of the unreacted vinyl acetate groups.

All the above peaks are also observed in the reaction product, making the analysis by FTIR somewhat difficult. Some indicative results can be ob-



**Figure 6** FTIR spectra for two spectral regions of SMA8/EVAL75 mixtures for 20 min (solid line) and 30 min (dotted line) mixing time.



**Figure 7** DSC thermograms of SMA8, EVA8, and their mixture (30 min mixing time).

tained if we compare the spectra of products taken at different reaction times, as shown in Figure 6.

It is observed in these FTIR spectra that there is a reduction in the absorbance of the hydroxyl peak since some hydroxyl groups of EVAL have reacted with the maleic anhydride groups of SMA8. This is confirmed by the simultaneous decrease in the anhydride carbonyl peaks at 1858 and 1780  $\text{cm}^{-1}$ . There is also an increase in the absorbance at 1735  $\text{cm}^{-1}$  due to the ester formed during the reaction.

Theoretically, it is possible to determine the extent of the reaction by measuring the anhydride carbonyl peak; but in practice, this is not possible due to the large overlap of this peak with other neighboring peaks, especially in SMA14 mixtures.

### DSC Study

From the copolymers used in this study, styrene/maleic anhydride copolymers are completely amorphous, showing only a glass transition temperature, which is 121.8°C for SMA8 and 134.4°C for SMA14, respectively. This is in accordance with the observation that a 1 wt % increase in maleic anhydride content causes a 2°C increase in the observed  $T_g$ .<sup>28</sup>

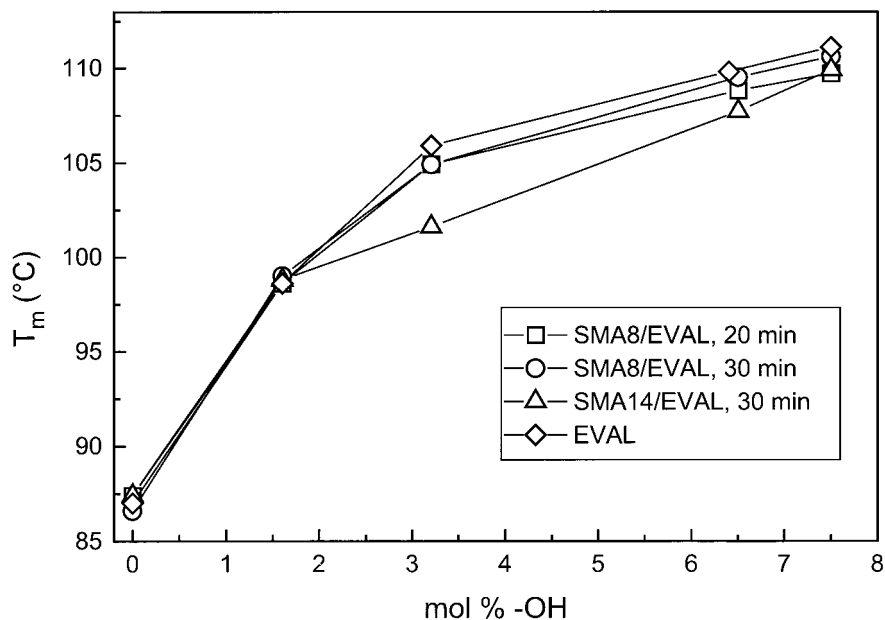
EVAL copolymers, on the other hand, appear to be semicrystalline, and their melting tempera-

ture is increasing with the extent of hydrolysis. Thus, while non-hydrolyzed ethylene/vinyl acetate copolymer has a melting point of 86.5°C, the melting temperature of the hydrolyzed samples rises to 98.5°C for the copolymer containing 1.6 mol % hydroxyl groups and up to 111°C for the copolymer containing 7.5 mol % hydroxyls. A similar trend is observed for the heats of melting. Thus, it seems that crystallinity is increasing with increasing hydroxyl content. This is expected since hydroxyls are capable of hydrogen bonding, which greatly facilitates crystallization.<sup>29</sup>

Figure 7 depicts the DSC thermograms of SMA8, EVA, and their mixture after a 30 min mixing time.

From this thermogram, it can be seen that no significant change occurs upon mixing since both  $T_g$  of SMA8 and melting temperature of EVA remain unchanged to within experimental error ( $\pm 1^\circ\text{C}$ ). In contrast, there is a small decrease in the melting temperature of SMA/EVAL mixtures compared to that of pure EVAL copolymers, as can be seen in Figure 8. This is probably due to the branch/crosslink formation between polymer molecules. Branching and especially crosslinking in polymers decreases crystallinity because they inhibit the free movement of chains. This inhibition makes it more difficult for the polymer to obtain a conformation favorable for crystallization



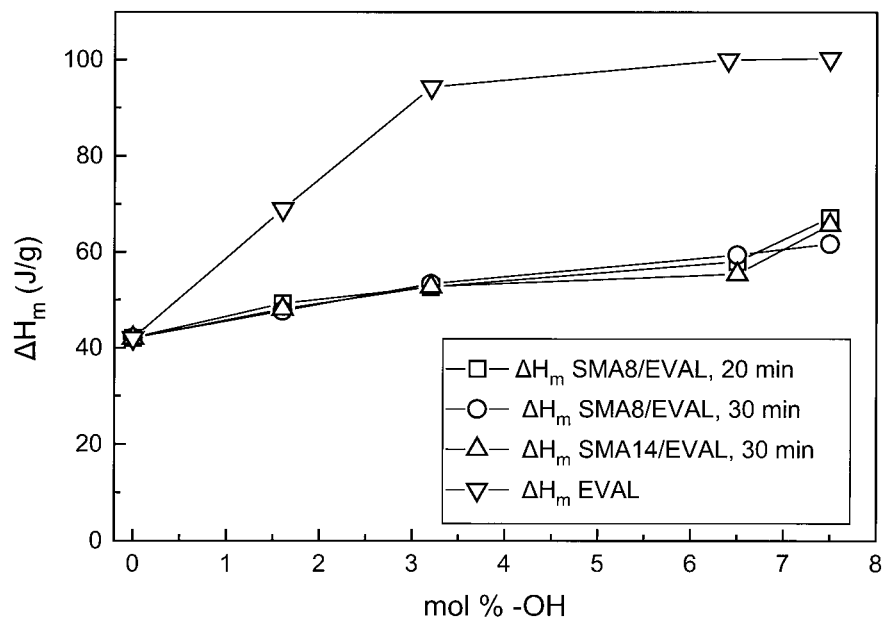


**Figure 8** Melting temperature diagram of EVAL mixtures with SMA8 and SMA14.

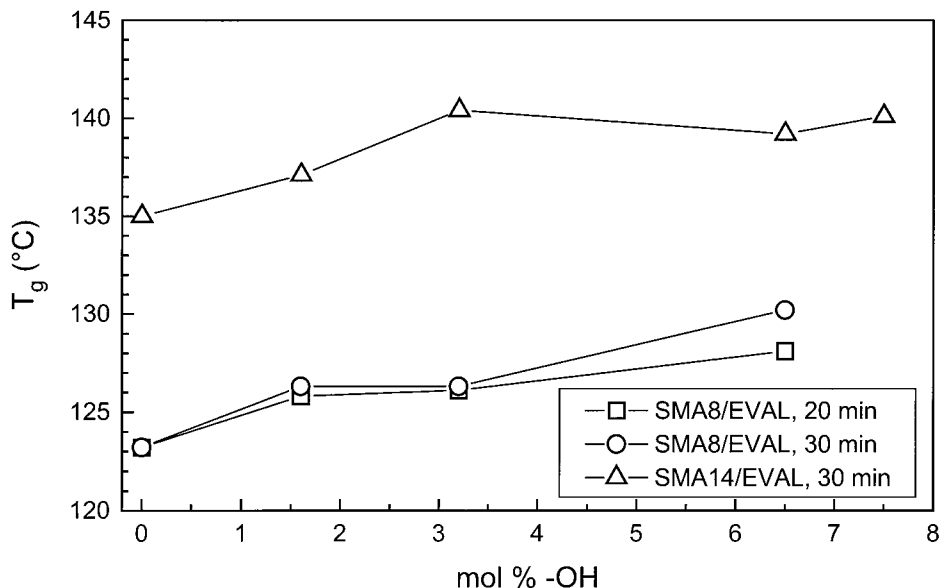
to take place. In EVAL16 mixtures, where there is a low concentration of hydroxyl groups, and, as a consequence, crosslinking is expected to be decreased, there is no significant change in  $T_m$ .

The decrease in crystallinity can also be concluded from the heat of melting of mixtures, as shown in Figure 9. It must be noted that the heat of melting of mixtures are normalized for EVAL

copolymer content by multiplying the raw heat of melting by a correction factor of  $100/(100-C)$ , where  $C$  is the content percentage of mixture in EVAL. Since all mixtures prepared had a 50 : 50 wt % composition, this factor is equal to 2 for all mixtures. Except for the SMA/EVA mixture, where  $\Delta H_m$  is almost equal to that of pure EVA (42.7 J/g), for the other mixtures, there is a significant reduction in



**Figure 9** Heats of melting of EVAL mixtures with SMA8 and SMA14.



**Figure 10** Glass transition temperatures of EVAL mixtures with SMA8 and SMA14.

heat of melting ranging from 30 to 40% compared to that of pure EVAL copolymers.

It is observed that the crystallinity of blends is increasing with increasing hydroxyl content of the EVAL copolymers used. This is due to the increasing crystallinity of pure EVAL copolymers with increasing hydroxyl content.

Glass transition temperatures of mixtures are shown in Figure 10. For EVA8 mixtures with SMA8 and SMA14, there is no change in  $T_g$  temperatures compared to that of pure SMA copolymers. However, in SMA mixtures with EVAL, there is a small increase in  $T_g$ s ranging from 2 to 6°C. This increase is apparently a consequence of crosslinking, which causes a decrease in chain mobility. It was not possible to determine the  $T_g$  of SMA8/EVAL75 mixtures since the glass transition is overlapped by the melting endotherm peak of EVAL polymer. This is not the case for SMA14 mixtures in which glass transition appears at higher temperatures and  $T_g$  is well separated from the melting peak.

## TGA

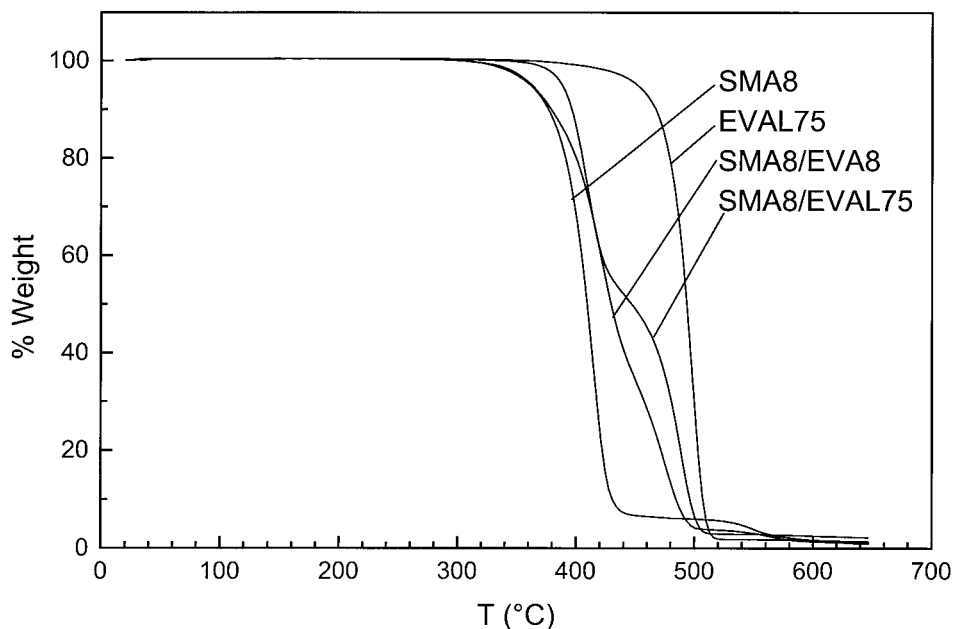
SMA copolymers are decomposed in two stages. The first stage takes place up to 430°C and involves mainly the polystyrene decomposition. The second stage appears to be mainly connected with maleic anhydride decomposition since the residue

after the first decomposition appears to be roughly equal to the maleic anhydride content of the copolymer. Thus, the residue is 8% w/w and 14% w/w for SMA8 and SMA14, respectively.

EVA decomposes in two stages. In the first stage, up to 350°C, it decomposes with evolution of acetic acid<sup>30,31</sup> with a weight loss of 14.6% w/w. The second step is attributed to the decomposition of the polyethylene fraction. For EVAL copolymers prepared from EVA hydrolysis, there are also two decomposition steps. However, weight loss in the first stage decreases with increasing hydrolysis extent. This is expected since the higher the hydrolysed fraction is, the fewer vinyl acetate groups will remain in the EVAL molecule.

Figure 11 depicts the TGA thermograms of the copolymers used and of SMA8/EVAL75 and SMA8/EVA8 mixtures.

SMA8/EVA8 mixture shows three decomposition steps in accordance with the corresponding steps of the component copolymers. SMA8 mixtures with EVAL16 and EVAL32 also show three decomposition steps with the last step lying above 580°C. This step is probably due to the presence of a significant amount of unreacted maleic anhydride groups in these mixtures, which finally decompose at this third stage. This is also the case for mixtures prepared with SMA14. Mixtures prepared from EVAL65 and EVAL75 show only two decomposition steps. The last decomposition step of maleic anhydride has been drastically sup-

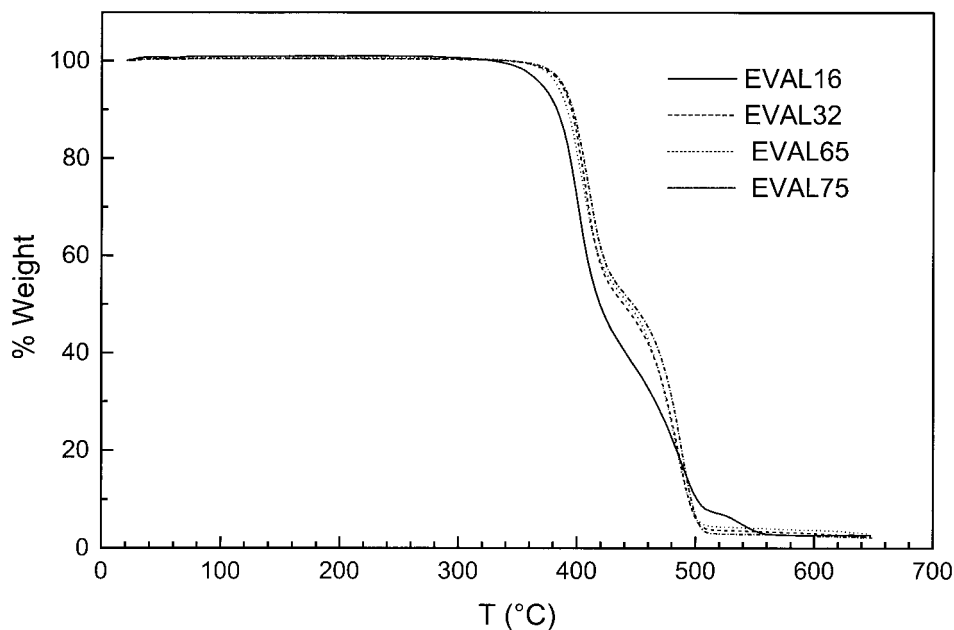


**Figure 11** TGA thermograms of SMA8, EVAL75, and SMA8/EVAL75 and SMA8/EVA8 mixtures.

pressed. This is an indication that in these mixtures, maleic anhydride has reacted to a much greater extent.

The decomposition onset temperatures of the mixtures are somewhat higher compared to the pure components, possibly because crosslinking

increases the thermal stability of the product. This is verified by the fact that mixtures prepared from EVAL copolymers with a high hydroxyl content (which leads to more crosslink formation); e.g., EVAL65 and EVAL75 appear to be thermally more stable, as shown in Figure 12.



**Figure 12** TGA thermograms of SMA8/EVAL mixtures (30 min mixing time).

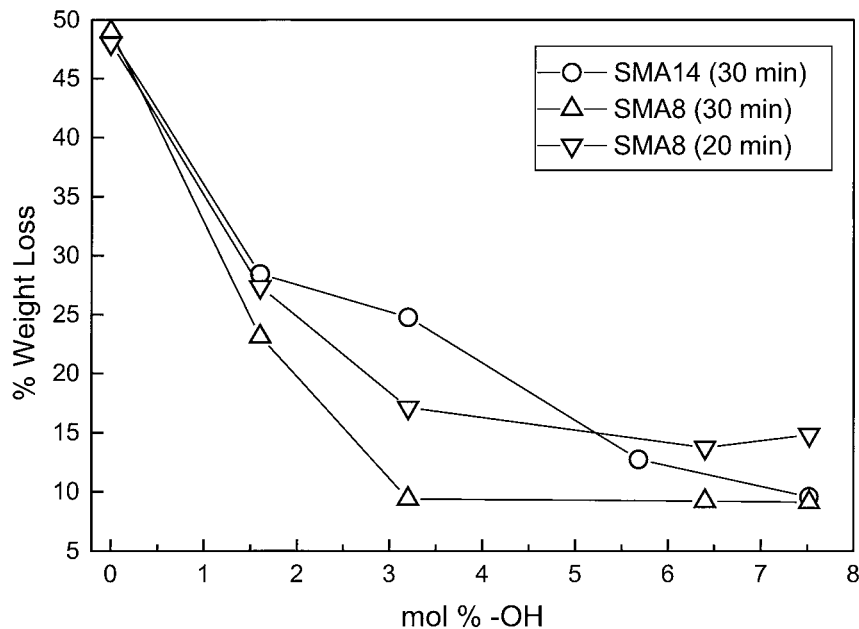


Figure 13 Acetone soluble fraction of SMA/EVAL mixtures.

### Extraction Results

After melt mixing, the samples were subjected to extraction with appropriate solvents in order to remove the unreacted copolymers and to determine the crosslinked fraction in each mixture.

The samples were initially extracted with acetone, which is a selective solvent for SMA.

Results for acetone extraction of samples are shown in Figure 13. From this diagram, it can be seen that for mixtures prepared from EVA, the extractable fraction is almost equal to the amount of SMA in the blend. This fact indicates that SMA and EVA do not react when blended.

In contrast, mixtures prepared from EVAL polymers show significantly lower extractable fractions. This means that a significant amount of SMA is incorporated in an acetone insoluble polymer. Mixtures prepared from EVAL with lower hydroxyl content (1.6 and 3.2 mol %) show a higher extractable fraction compared to those with 6.5 and 7.5 mol % hydroxyl. This is probably a result of a lower extent of reaction due to the fact that the lower concentration of reactive hydroxyl groups leads to leaving more unreacted SMA molecules.

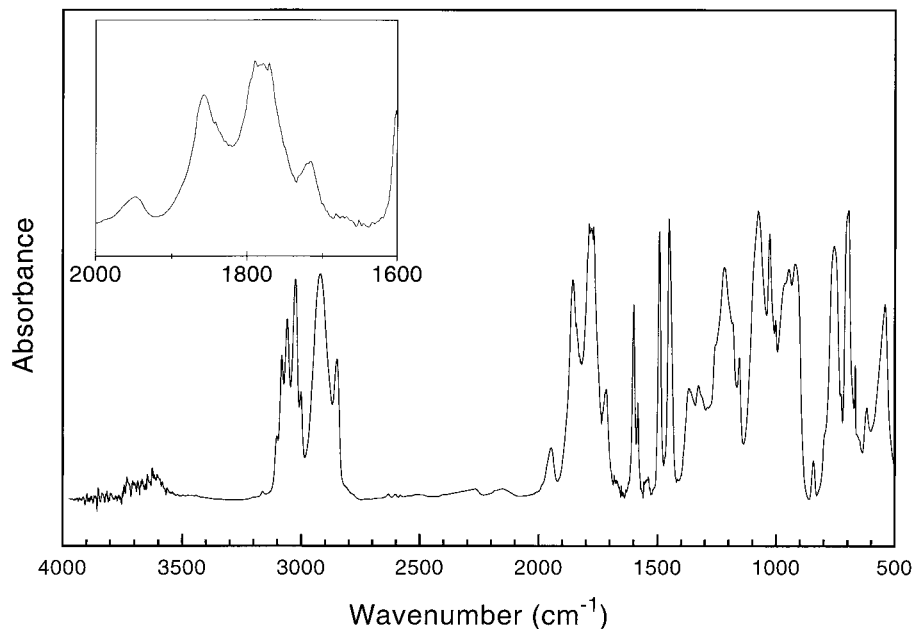
Mixing time also affects the extractable fraction. Mixtures prepared with a 30 min mixing time have a lower extractable fraction compared to those with 20 min mixing time, indicating that the reaction has proceeded to a greater extent in the former. This is in accordance both with the

torque reading, which shows a continued torque increase even after 20 min of mixing, and with FTIR spectra, which show a larger decrease in anhydride carbonyl peak for the samples mixed for 30 min.

In SMA14 mixtures, where there is an excess of maleic anhydride groups, especially in mixtures with EVAL16 and EVAL32, there is a smaller amount of reacted SMA polymer, and the extractable fraction is larger.

The acetone soluble fractions were evaporated to dryness and weighted. The solids content of the solutions obtained were almost equal to the weight loss of the polymer films subjected to extraction. The solid residues were subsequently studied by FTIR after drying at 80°C under vacuum overnight. Figure 14 shows a typical FTIR spectrum of an acetone extractable fraction. In the FTIR spectrum, the anhydride carbonyl peak is prominent, but a new peak appears at 1717  $\text{cm}^{-1}$ . Since the spectra lack any EVAL characteristic peaks (e.g., at 718–730 and at 1465  $\text{cm}^{-1}$ ), this peak cannot be due to a new group formed by a reaction; but rather, it can be attributed to carboxyl groups formed from anhydride hydrolysis during extraction. DSC and TGA thermograms of the residues also appear to be identical to those of the initial SMA copolymers.

From the above, it is evident that, actually,



**Figure 14** FTIR spectrum of acetone extractable fraction. (A magnification of the carbonyl area is shown in the insert.)

only a fraction of the functional groups react. Also, the extent of the reaction is determined not only by the concentration of the reactive groups but from their molar ratio as well.

The acetone insoluble residues were also studied using FTIR, DSC, and TGA.

The FTIR study showed that there were no significant differences in the extracted samples compared to the unextracted ones, except for a slight reduction in SMA characteristic absorbances due to the extraction of unreacted SMA. No significant differences were detected in  $T_g$  and heats of melting. In TGA, there is only a partial reduction in the first stage weight loss due to the reduction of SMA content in acetone extracted samples.

Acetone insoluble fractions were extracted for one week with toluene at room temperature and showed no significant weight loss, an indication that unreacted SMA was completely extracted by acetone. Thus, this fraction is expected to contain the product of reaction between SMA and EVAL copolymers, along with unreacted EVAL copolymers, which are insoluble in acetone.

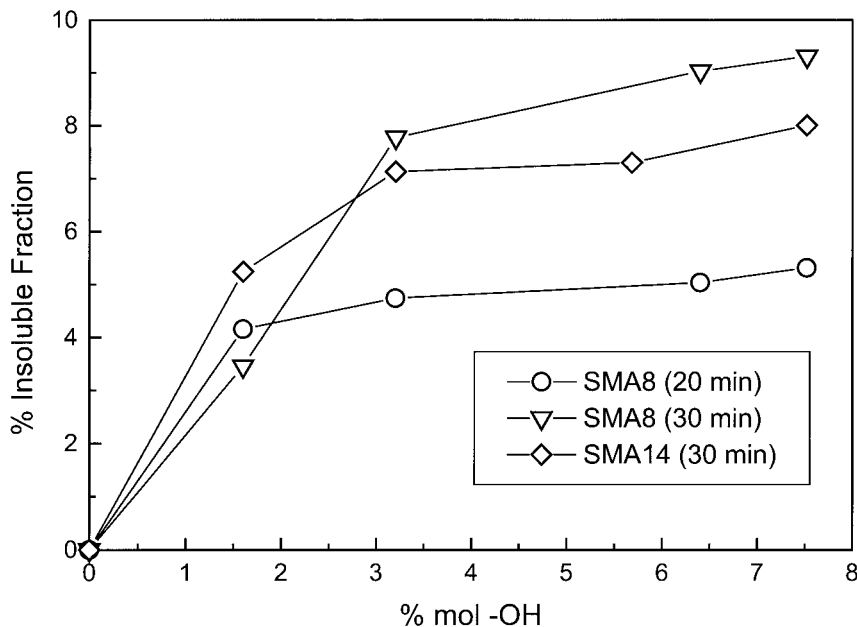
Acetone insoluble fractions were subsequently extracted with hot toluene. It is not possible to determine from these extractions the unreacted EVAL since the reaction product is to a great extent soluble in toluene as well. FTIR spectra of

the material dissolved in toluene confirm that a reaction took place since they contain the characteristic peaks of styrene units, indicating that polystyrene has been incorporated into the material structure. Anhydride characteristic peaks also appear in the above spectra, and this is an indication that some part of the anhydride groups has not reacted.

There is an insoluble fraction for extracted samples attributed to a highly crosslinked material. The toluene insoluble fraction is presented in Figure 15.

No insoluble fraction was detected in the SMA8/EVA8 and SMA14/EVA8 mixtures since no reaction has occurred and no crosslinked products have been formed. The insoluble fraction in PEVAL/SMA blends was lower in mixtures prepared after 20 min mixing time compared to that of mixtures prepared after 30 min mixing time. This is a further indication that the crosslinking reaction has proceeded to a greater extent in the latter. This is in accordance with the above mentioned acetone extraction experiments.

From Figure 15, it can also be concluded that the insoluble fraction increases with increasing ratio of reactive groups. This in turn leads to the conclusion that, in this case, the intermolecular reaction takes place to a higher extent.



**Figure 15** Toluene insoluble fraction of SMA/EVAL mixtures versus OH content of EVAL copolymer.

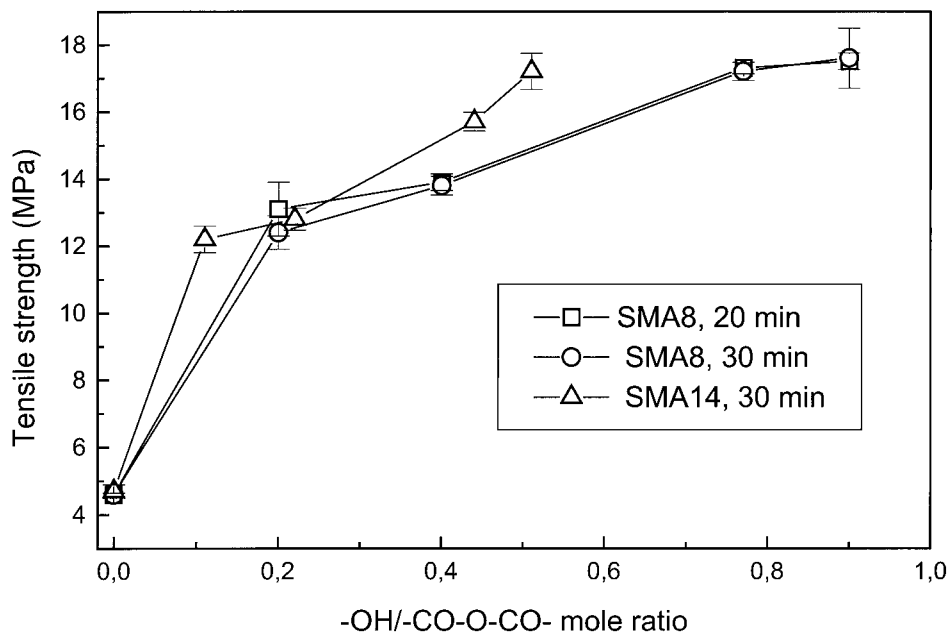
### Mechanical Properties

Blends that contain roughly equal proportions of polyethylene and polystyrene have the strength of polyethylene and the brittleness of polystyrene.<sup>4</sup> A mixture of LDPE/PS 50 : 50 w/w, prepared by the same Rheomix unit, had a tensile strength of 6.03 MPa and an elongation at break of 21.3%. Corresponding mixtures of EVA8 with SMA8 and with SMA14 present lower tensile strengths, which are 4.60 MPa and 4.67 MPa, respectively.

Compared to EVA/SMA, mixtures prepared from functionalized copolymers have higher tensile strengths, which are three times higher in mixtures prepared from EVAL16 and four times higher in mixtures prepared from EVAL75, as can be seen in Figure 16. Error bars in the diagram represent the 95% confidence interval for the respective measurement. The same applies for all other diagrams of mechanical properties. From this diagram, it can also be observed that SMA8 mixtures prepared with different mixing times, that is, 20 and 30 min, show approximately the same tensile strengths. Tensile strengths of SMA14/EVAL mixtures appear to be higher compared to the corresponding SMA8/EVAL mixtures. Tensile strength also increases with increasing  $-\text{OH}/-\text{CO}-\text{O}-\text{CO}-$  mol ratio for all mixtures prepared. To a great ex-

tent, this increase is due to the reaction occurring between the two copolymers, which produces branched and crosslinked polymer chains. In fact, the higher the hydroxyl content of the EVAL polymer is (leading to a higher degree of branching and crosslinking as verified from extraction experiments), the higher the tensile strength is. The increase is also partly attributable to the higher crystallinity observed with increasing hydroxyl content as verified from DSC. It is well known that crystallinity increases tensile strength.<sup>32</sup> Thus, mixtures prepared from EVAL65 and EVAL75 show the highest tensile strength.

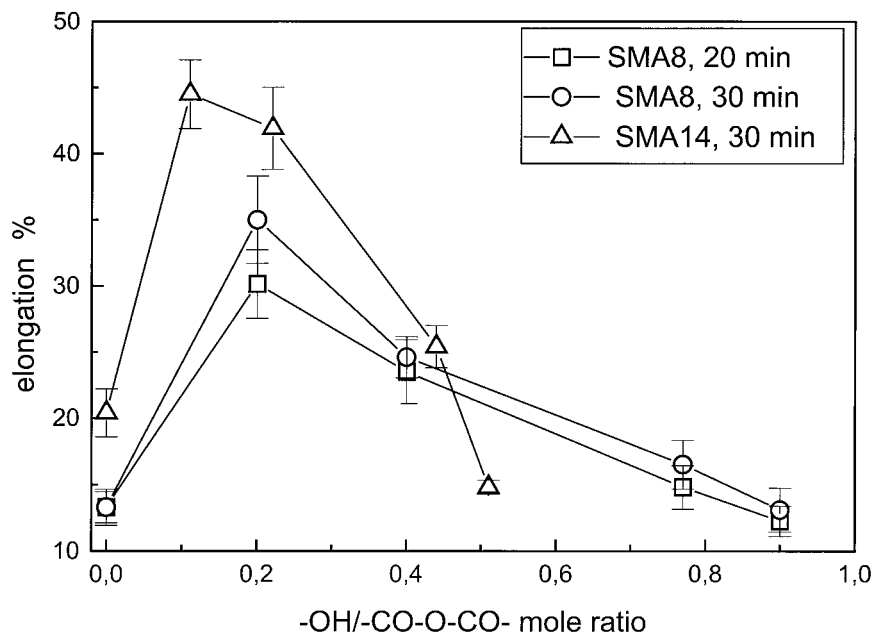
Elongation at break follows the opposite trend from that of tensile strength after an initial increase at low  $\text{OH}/-\text{COCO}-$  molar ratio, as shown in Figure 17. Thus, mixtures prepared from low hydroxyl content EVAL show a maximum in the elongation at break. In fact, the elongation at break of mixtures consisting of EVAL and SMA8 with a 1.6 mol % hydroxyls (EVAL16) lies between 30–35%, which represents a threefold increase in elongation at break compared to that of SMA8/EVA8 mixture. The elongation at break for the SMA14/EVAL16 mixture is 45%. This value is almost two times higher compared to that of the parent SMA14/EVA8 mixture. Elongation at break also de-



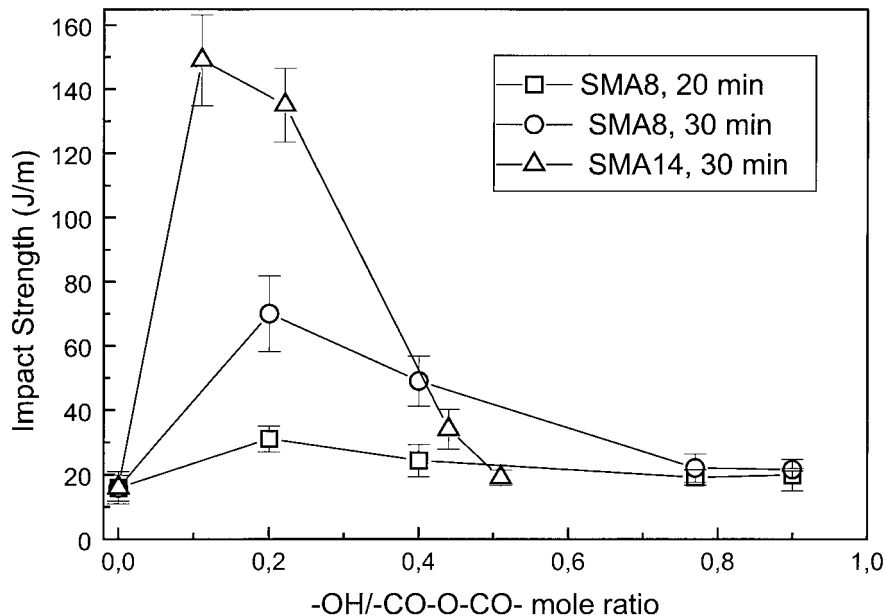
**Figure 16** Tensile strength diagram of samples versus hydroxyl/anhydride molar ratio of SMA/EVAL copolymers.

creases with increasing hydroxyl concentration in the SMA14 mixtures. This is due to the concomitant increased extent of crosslinking that takes place. Crosslinked polymers have lower elongation at break due to the decreased mobility of polymer chains.<sup>32</sup>

A trend similar to that of elongation at break is observed for impact strength, as shown in Figure 18. The impact strength of SMA8/EVA8 and SMA14/EVA8 blends (with zero —OH content) is 16 J/m. Concerning the SMA/EVAL blends, after an initial increase at low —OH/—COOCO— mo-



**Figure 17** Elongation at break diagram of samples versus hydroxyl/anhydride molar ratio of SMA/EVAL copolymers.



**Figure 18** Impact strength versus hydroxyl/anhydride molar ratio of SMA/EVAL copolymers.

lar ratio, there is a decrease in impact strength with increasing  $-\text{OH}/-\text{CO}-\text{O}-\text{CO}-$  mol ratio. This initial increase in impact strength and elongation at break follows the increase in tensile strength. At higher molar ratio, the decrease in impact strength and elongation at break with increasing  $-\text{OH}/-\text{CO}-\text{O}-\text{CO}-$  mol ratio is opposite to the trend observed for tensile strength. This latter phenomenon is often observed in rubber toughened polymers.<sup>33</sup> When impact strength, elongation at break, work to break, and fracture toughness are all increased severalfold, there is an inevitable reduction in tensile strength and in modulus too.

From Figure 18, it can be seen that mixtures prepared from SMA14 have a higher impact strength compared to that of samples prepared from SMA8 when  $-\text{OH}/-\text{CO}-\text{O}-\text{CO}-$  mol ratio lies below 0.4. For mol ratios above 0.4, however, the trend is reversed. It is well known that the stoichiometry of the hydroxyl-anhydride reaction is 1 : 1. In mixtures with  $-\text{OH}/-\text{CO}-\text{O}-\text{CO}-$  mol ratio  $< 0.4$ , the shortage of hydroxyl groups is greater than in those with a mol ratio  $> 0.4$ . Thus, there are more unreacted anhydride groups in the final product. As shown before from extraction experiments, the degree of crosslinking in these mixtures depends on the extent of the reaction. A certain degree of crosslinking between the two polymers is desirable since it can improve compatibility of immiscible polymers.

Improved compatibility improves the end use properties, including impact strength. As crosslinked products are concerned, however, further crosslinking is undesirable because it decreases impact strength, as can be observed in Figure 18 for mole ratios  $> 0.4$ .

Mixing time also plays an important role in impact strength, as can be seen from the same figure. SMA8/EVAL mixtures prepared with a mixing time of 30 min have higher impact strength compared to SMA8/EVAL mixed for 20 min.

As a conclusion, a maximum is observed for elongation at break, and impact strength for  $-\text{OH}/-\text{CO}-\text{O}-\text{CO}-$  mol ratio close to 0.2. This represents an optimum composition region as far as mechanical properties of the crosslinked products are concerned since both elongation at break and impact strength have a maximum, and tensile strength also shows an increased value compared to EVA8/SMA mixtures.

## CONCLUSIONS

Styrene/maleic anhydride copolymers were melt blended with ethylene/vinyl alcohol copolymers containing different amounts of vinyl alcohol. The temperature and rotation speed in the mixer, as well as the molecular weights of the mixed copolymers, were kept constant throughout this study.



During melt processing, there is a reaction occurring between maleic anhydride and hydroxyl groups, resulting in the formation of branched and crosslinked polymers. This is verified by FTIR, DSC, and extraction experiments, which show a material with significantly different properties compared to the initial components.

The reaction extent increases with increasing hydroxyl/maleic anhydride molar ratio and mixing time. The overall concentration of the functional groups in the mixture plays also a significant role in the structure and the properties of the produced blend. The best combination of mechanical properties is observed for low —OH/—CO—O—CO— ratios.

The products formed during this reactive blending contain both polyethylene and polystyrene branches and thus have the potential to be used as compatibilizers in PE/PS blends. This can be accomplished either by directly mixing them with PE and PS or by forming the product *in situ* during processing by adding SMA and EVAL in the PE/PS mixture before melt blending. Preliminary experiments have shown that, in some cases, use of the prepared polymers as compatibilizers in PE/PS blends improves the mechanical properties of the final products. This will be the subject of a forthcoming publication.

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