Morphology and Mechanical Properties of Reactive Compatibilized Polystyrene/Ethylene–Vinyl Acetate–Vinyl Alcohol Blends

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ABSTRACT: A reactive compatibilizer, styrene–maleic anhydride (SMA) was used to compatibilize the blends of polystyrene (PS) and ethylene–vinyl acetate–vinyl alcohol (EVAOH), which was synthesized from ethylene–vinyl acetate (EVA) using transesterification reaction. The compatibilized blends with different compositions were prepared using a twin-screw extruder and injection molded into the required test specimens. Morphology of Charpy impact-fractured surfaces, tensile, and impact properties of the blends were investigated. Fourier-transform infrared spectroscopy (FTIR) was also applied for specific samples to elucidate the presence of the functional groups reaction necessary for reactive compatibilization. The results of the ternary PS/EVAOH/SMA blends illustrate that the addition of SMA as a compatibilizer slightly reduce the elongation at break. From the impact-fractured surfaces of the blends, it is evident that the morphology developed sizable pores when SMA was added into the blends. This might be attributed to the residual octanol-1, produced from the synthesis of EVAOH, as there is a possibility of a reaction between hydroxyl groups in the octanol-1 and the anhydride groups in the SMA. This disrupted the stability of the morphology and resulted in the decrease in the elongation, and hence, the tensile toughness. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 209–217, 2002

Key words: tougheness; mechanical properties; morphology

INTRODUCTION

Reactive compatibilization is commonly used for the toughening of polystyrene (PS).[1–10] The reactive compatibilization uses the reactive functionalities present in the polymers to form graft or block copolymers *in situ* during processing. These copolymers act as compatibilizers by reducing the interfacial tension and increasing the adhesion between the phases, which allows finer dispersion and more stable morphology to be produced. This method of compatibilization provides a viable approach in compatibilizing the binary blends of PS and ethylene–vinyl acetate copolymer (EVA). However, based on our previous studies on the ternary blends of PS, EVA, and styrene–maleic anhydride (SMA), there is no evidence of reaction between the anhydrides and acetates.[11]

Therefore, we examine a more established reaction between hydroxyl and anhydride functional groups in this study. Tselios et al.[12] had studied the blends of poly(ethylene-*co*-vinyl alcohol) (EVAL) and SMA. They concluded that a reaction occurred between maleic anhydride (MA) and hydroxyl groups, resulting in the formation of branched and crosslinked polymers. The conclu-
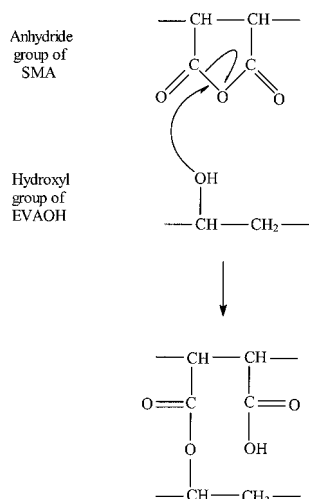
Figure 1 Reaction scheme between anhydride and hydroxy functional groups to produce an *in situ* compatibilizer.[12]

sion was verified by Fourier-transformed infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and extraction experiments, which showed the emergence of a new material significantly different compared to the initial constituents. However, for the blends of SMA and EVA, there were no functional groups capable of reacting. They found that the best combination of mechanical properties was observed for blends with a low molar ratio of hydroxyl to anhydride functional groups. Flores et al.[13] also observed similar functional group reaction from their investigation on the blends of ethylene–vinyl acetate–vinyl alcohol (EVAOH) and SMA.

Based on the above, a reactive compatibilization using SMA in the blends of PS and EVAOH was explored. A functional group reaction between the anhydrides in SMA and hydroxyl in EVAOH is proposed and shown in Figure 1. This results in branched and crosslinked reaction between the two polymer chains during melt processing. Thus, an *in situ* compatibilizer with one side having a chain of SMA and the other EVAOH is initiated. As mentioned previously, SMA is partially miscible in PS due to their similarity in chemical structure and composition. In this way, the compatibilizer could enhance interfacial adhesion between the brittle PS phase and dispersed rubbery phase of EVAOH. With compatibilization between the two phases, PS could be toughened.

EVAOH could be obtained by functionalizing EVA with hydroxyl groups through a transesteri-

fication reaction that results in a partial conversion of the acetate groups as shown in Figure 2. Investigations on the transesterification of molten EVA in the presence of paraffinic alcohols and basic catalyst were reported by Lambla et al.[14] and Hu et al.[15] They succeeded in achieving high conversions of the ester groups to secondary alcohol by using a mixer and extruder. Their experiments involved various kinds of alcohols and two different catalysts. Sodium methoxide was found to be a powerful catalyst for the equilibrated transesterification reaction. However, side reactions, such as crosslinking with low molecular weight alcohols and hydrolysis of the catalyst followed by partial saponification of the EVA were observed. On the other hand, dibutyltin dilaurate (DBTDL) is known to be an efficient catalyst that does not promote any side reaction. In this study, one of the successful compositions was adopted and used for synthesizing EVAOH. The composition of 30 wt % of octanol-1 and 3 wt % of DBTDL was chosen to transesterify EVA265 into EVAOH. The synthesized material was subsequently used as the elastomeric modifier for PS.

In this study, 2, 5, and 10 wt % of SMA7 and SMA14 were added to the PS/EVAOH (90 : 10 wt %) blend, respectively. Extrusion and injection molding were carried out at 200°C. Tensile and Charpy impact tests were performed according to ASTM D638 and ASTM D256, Test Method B. The morphologies of the blends were examined using a scanning electron microscopy (SEM). FTIR was used to ascertain the transesterification reaction in the synthesis of EVAOH.

EXPERIMENTAL

Materials

The system investigated in this study consists of a matrix of PS (MFI of 8.0 dg/min) supplied by Dow
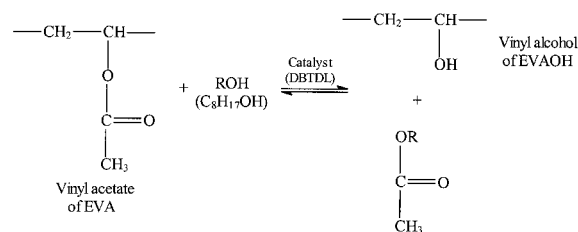

Figure 2 Transesterification reaction of EVA into EVAOH with the presence of an alcohol (octanol-1) and a catalyst.[15]

Table I Physical Properties of PS and EVA 265

Properties	ASTM Method	PS	EVA 265
Melt flow rate, condition G (dg/min)	D-1238	8.0	3.0
Zero shear viscosity (Pa · s)		5.6×10^4	1.2×10^4
Density @ 23°C (kg/m³)	D-1505	—	955
Hardness, Shore A-2 Durometer, 10 s	D-2240	—	83
Softening point, ring and ball	E-28		
(°F)		—	340
(°C)		—	171

Data obtained from technical data sheets except the zero shear viscosity.

Chemical Company (STYRON 666H); a minor phase of EVAOH, which was synthesized from EVA with MFI of approximately 3.0 dg/min, manufactured by DuPont (ELVAX 265, VA content of 28.0 wt %), and two commercial compatibilizers purchased from Aldrich (SMA7 and SMA14). The details of these polymers and compatibilizers are summarized in Tables I and II, respectively. The mechanical properties of the reactive compatibilized PS/EVAOH blends studied in this project were compared with a commercial high-impact polystyrene (HIPS) supplied by Dow Chemical Company (STYRON 470).

Preparation of Blends and Test Samples

The EVAOH was prepared using a Haake Rheomix 600 batch mixer with a Haake Rheocord 90 drive system. For synthesis of material in the mixer chamber, a Haake Rheomix 600 with a capacity of 69 cm³ was used with a Haake Fisons Rheocord Drive 90 unit. However, the volume of materials placed into the chamber was recommended to be below 70% of its capacity, i.e., 50 cm³. The ingredients of 40 g of EVA265, 12 g of octanol-1 and 1.2 g of DBTDL were poured into the mixer after the temperature at the three mix-

Table II Physical Properties of Compatibilizers

Properties	ASTM Method	SMA7	SMA14
MFI (dg/min)	D-1238	1.7	1.9
Wt % of styrene	—	93	86
Wt % of MA	—	7	14
Hardness, Rockwell L	D-785	108	108

Data obtained from the technical data sheets.

ing sections had reached 170°C. The temperature was then maintained throughout the mixing process. Roller blades were counterrotating with the drive set at 50 rpm and the process was continued for 30 min. The synthesized EVAOH was cut into smaller pieces after removal from the mixing chamber.

The 2, 5, and 10 wt % of SMA7 and SMA14 were added to the PS/EVAOH (90 : 10 wt %) blends (denotes as P10EVAOH/5SMA7 if 5wt% of SMA7 was added to the binary blend of P10EVAOH, etc.). The materials were mixed thoroughly before the mixture was poured into the hopper of the corotating twin-screw extruder (Haake-Rheocord 90). The rotor speed was set at 10 rpm at a temperature of 200°C. The die used at the exit of the extruder had a diameter of 1.5 mm. The extrudate passed through a water bath before it was pelletized. The dried pellets of the blend were reintroduced to the hopper for second extrusion. The blend was extruded for a total of four times with rotor speeds of 5, 2, and 3 rpm, respectively. This was done to increase the residence time and opportunities for reactions to take place. The extruded blends were then quenched in a water bath and subsequently pelletized. The pelletized blends were then dried in the oven for 24 h at 60°C and injection molded using the Manumold 77/30 at 200°C to produce ASTM standard test samples for tensile and Charpy impact testing.

Mechanical Testing

Tensile testing (ASTM D638) was performed using dumbbell samples at room temperature (25°C) on the Instron 5566 tensile testing machine using a 10 kN load cell at a crosshead speed of 5 mm/min. An extensometer of 50 mm gauge length was used to accurately measure the strain.

From the stress–strain curves, various tensile properties such as tensile strength, tensile yield strength, tensile modulus, tensile toughness, and elongation at break were obtained. The average and standard deviation of 10 test pieces of each blend were determined.

Charpy impact test (ASTM D256, Test Method B) was conducted at room temperature (25°C) using notched test samples of notch width 4 mm using the Dynatup POE2000 pendulum impact test machine. A pendulum weight of 0.898 kg and strike angle of 90° was used. The average and standard deviations of 10 test pieces for each sample were determined.

Morphological Studies

The Charpy impact-fractured surfaces of the test samples were cut to a thickness of about 5 mm and attached to the base plate using carbon tape. They were then gold coated by the gold spluttering machine and studied on a JEOL scanning electron microscope (JSM-5410LV), at an EHT of 20 kV and a fixed magnification of 5 k for consistency to facilitate comparison of droplet size.

From the SEM micrographs, the microstructure of the blend systems was examined along with the qualitative effects of the compatibilization. Qualitatively, the average droplet size was taken to observe the effects of compatibilizer. This was done by measuring the droplet or minor phase particle diameters from the micrographs (by using an image analyzing software, Image-Pro Plus, version 2.0) and taking the average and standard deviation of these measurements.

Fourier-Transform Infrared Spectroscopy (FTIR)

To investigate the chemical reactions between the functional groups, FTIR (Nicolet Megra-IR 560ESP) was used. The FTIR provides evidences on the molecular structure of the materials as certain molecular functional groups possess vibration coupling at predictable bands of characteristic frequencies. Empirically, the position, intensity, and width of absorption for a vibrational spectrum provide the correlation to a known molecular group. In this study, FTIR was used to ascertain the transesterification reaction in the synthesis of EVAOH. The EVA265 and EVAOH were made into thin films by stretching the material at high temperature of 170°C. The chamber of the spectroscope was purged with nitrogen to remove carbon dioxide (CO_2). The infrared beam was passed through the film, and the FTIR spectrum was determined for a wave number ranging from 4000 to 400 cm^{-1}.

RESULTS AND DISCUSSION

Mechanical Properties

Comparing the stress–strain curves in Figure 3, the binary blend of PS/EVAOH (90 : 10 wt %) (denotes as P10EVAOH) achieves higher elongation compared to the blend of PS/EVA265 (90 : 10 wt %) (denotes as P10E265). However, the tensile strength and modulus is sacrificed for the increase in the toughness. The tensile toughness for the blend of P10EVAOH is still below that of the commercially available HIPS.

The tensile strength, tensile yield strength, and tensile modulus for the blends with addition of SMA in the P10EVAOH blend are shown in Figures 4(a)–(c). There are no marked changes in the strength, although for blends with 10 wt % SMA, there is a slight increase in the strength compared to the binary counterpart. This was explained earlier by the increase in the brittle phase with the addition of SMA, which leads to higher strength in the blends.[11] The tensile modulus has not changed significantly, as shown in the stress–strain curves in Figure 5.

The elongation at break and tensile toughness for the blends are shown in Figures 4(d) and 4(e), respectively. The deviation from the maximum and minimum values obtained for the blends are shown as error bars in the figures. From the results, it could be seen that the reduction in the elongation and toughness is more obvious in blends with addition of SMA7 than SMA14. These results seem to indicate that the proposed reaction between SMA and EVAOH may exist as SMA14 has more opportunities for reactions compared to SMA7.

The comparisons for their elongation at break when SMA7 was added to the blends containing P10E265 and P10EVAOH are shown in Figure 6. The figure suggests that EVAOH is a more suitable material compared to EVA265 for the reactive compatibilization in a PS/EVA blend system.

The results on Charpy impact strength of the blends are shown in Figure 4(f). The blends possess impact strength that is even lower than that of the PS (7.79 J/m). However, it should be noted that the addition of SMA marginally increases the impact properties, and this will be correlated to the morphology of the blends, which will be discussed below.
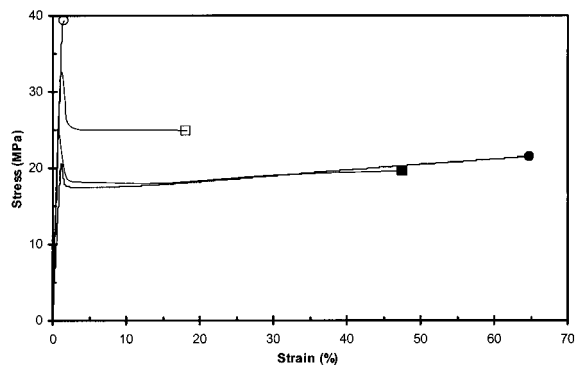
Figure 3 Tensile stress–strain curves of binary blends in comparisons with PS and HIPS (○—PS; ●—HIPS; □—P10E265; ■—P10EVAOH).

Morphological Studies (SEM)

The morphology of the binary blend, P10EVAOH, is shown by the Charpy impact-fractured surface in Figure 7(a). The particles are dispersed in stable morphology with mean diameter of less than 1 μm. As mentioned previously, an optimum rubber
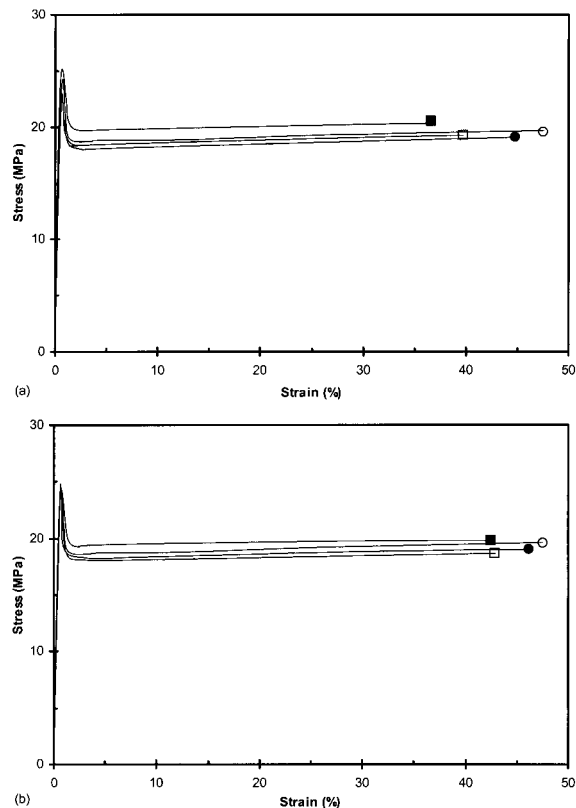

Figure 4 Tensile stress–strain curves for blends of P10EVAOH with varying content of (a) SMA7 and (b) SMA14 (○— 0 wt % SMA; ●—2 wt % SMA; □—5 wt % SMA; ■—10 wt % SMA).
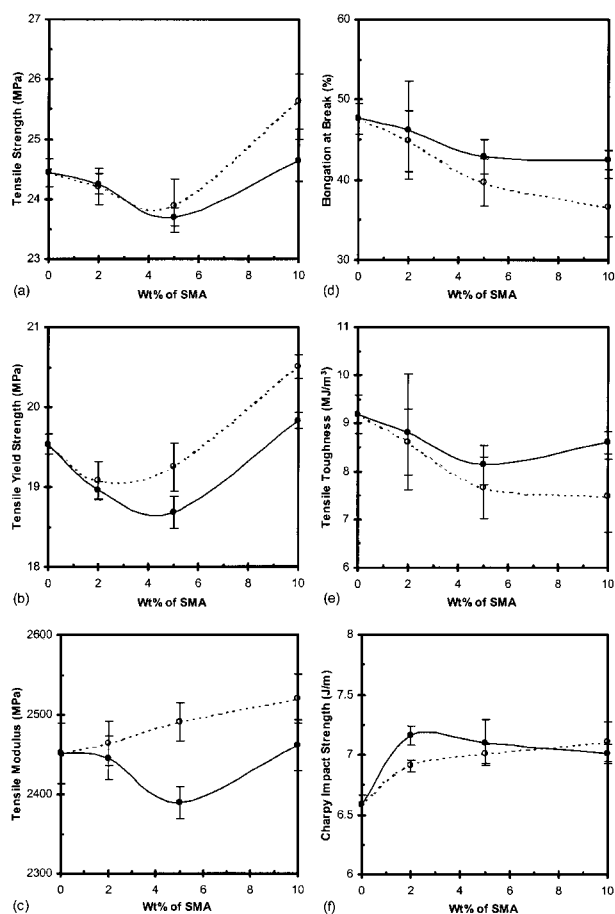

Figure 5 Mechanical properties of compatibilized P10EVAOH blends as functions of the type and content of SMA (○—SMA7; ●—SMA14).

particle size must be satisfied for impact modification. Thus, the particles, in this case, might be too small to enhance the multiple craze formation for impact toughening of PS. The phases seem to
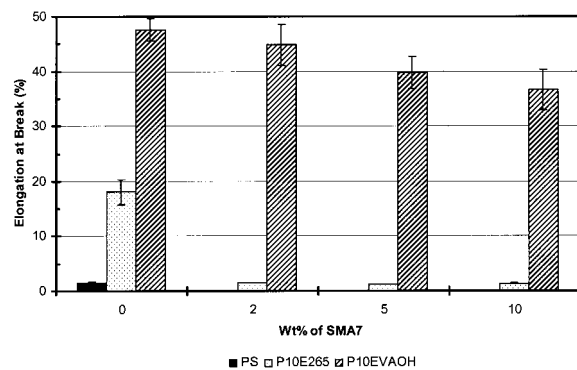

Figure 6 Comparisons of elongation at break between the blends of P10E265 and P10EVAOH with different contents of SMA7.
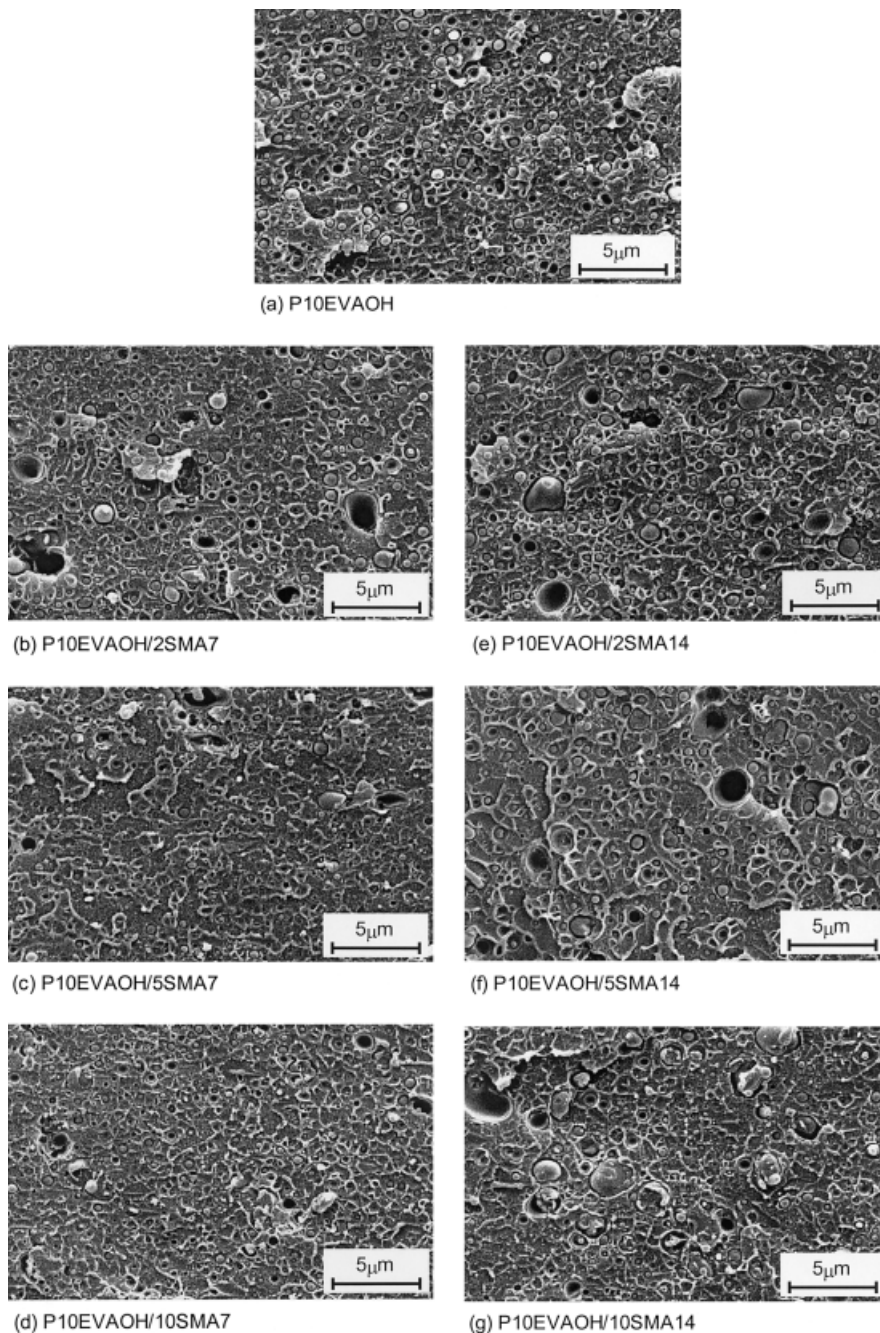
Figure 7 SEM micrographs of Charpy impact-fractured surface for binary and ternary blends of P10EVAOH and SMA.

lack adhesion as the rubber particles are in their un-deformed spherical shape. These observations correlate with the poor impact strength observed for the blend of PS and EVAOH.

The morphology of the blends with the addition of SMA in P10EVAOH becomes unstable, as shown in Figures 7(b)–(g). In general, sizable pores and large inclusions are evident on the

Charpy impact-fractured surfaces. The pores are stress concentration sites, which can promote rapid fracture through the matrix. The rubber particles thus play a minor role in the deformation of the materials. As such, fewer droplets are seen from the minor dispersed particles of these blends compared to their binary constituents. The cause of the pores developed in the blends might

be due to the reactions between the unextracted octanol-1, after the synthesis of EVAOH, and anhydrides in the SMA. This results in the development of foreign compounds, which can cause disruptions to the stability of the morphology that is responsible for the decline in the tensile toughness and the Charpy impact strength.

The effect of compatibilizers on the phase morphology could be correlated to the interfacial tension.[2,3,7,8,16,17] Blends with higher interfacial tension gave coarser phase morphologies that are unstable and that tend to coalesce. The tendency of the melt to coalesce is depressed by compatibilizers, which concentrate at the interface and act as emulsifiers to reduce the interfacial tension. In this case, when the blend of P10EVAOH has already developed a morphology with particle size that is smaller than the optimum, the base composition (90 wt % PS and 10 wt % EVAOH) may not be suitable for use for compatibilization. If compatibilization between the phases is achieved, the particle size would have been further reduced or at least remain unchanged as a good compatibilizer can stabilize the morphology and thus prevent coalescence. Thus, a higher composition of rubber content should be present in the blend, so that compatibilizing the blends would ideally reduce the dispersed particle size to the optimum value and become more effective in impact modification.

Fourier-Transform Infrared Spectroscopy (FTIR)

Comparing the spectra of EVA265 [Fig. 8(a)] and EVAOH [Fig. 8(b)], the EVAOH having an additional secondary alcohol (OH) can be identified. The broad band seen at around 3450 cm^{-1} represents the stretching of OH group. With this, the presence of alcohol is confirmed. Nevertheless, the hydroxyl band is contributed partially by the presence of any unextracted octanol-1. The characteristic group frequencies for stretching of secondary alcohol of C—O have an absorption band from 1150 to 1030 cm^{-1}.[18] For this region, the spectra of EVA265 and EVAOH exhibit a shift in the peak from 1125 to 1128 cm^{-1}. This suggests that a successful transesterification reaction on EVA has occurred. The absorption peak at around 1740 cm^{-1} represents the ester carbonyl groups of vinyl acetate. Because similar intensity in the peak of 1739 cm^{-1} for both spectra was obtained, this implies that the degree of conversion is not high.

Unlike the previous study on the blend system of PS/EVA/SMA,[11] the reactions between the functional groups could not be readily identified using FTIR. Given the reaction that had occurred, there would be a reduction in the absorption peaks of cyclic anhydride, because some hydroxyl groups of EVAOH would have reacted with the anhydride groups of SMA. This will correspond to a simultaneous decrease in the characteristic anhydride carboxyl peaks at 1858 and 1780 cm^{-1}. There should also be an increase in the absorption peak at around 1735 cm^{-1} due to the ester formed during the reaction as shown in Figure 1. However, in practical situations the spectra obtained are usually qualitative in nature, and could not be readily used to identify small changes in the intensity of the absorption peaks.

CONCLUSIONS

The reactions between the functional groups, hydroxyl and anhydrides, for the compatibilization of the blends of PS, EVAOH, and SMA was investigated. The EVAOH was synthesized by melt mixing of EVA265, octanol-1 and DBTDL, at a prescribed composition.

The synthesis of EVAOH from EVA265 via the transesterification reaction was identified from the distinctly different tensile curves for blends of similar composition. Blends of PS with EVAOH yield the higher elongation compared to that with EVA265. The comparison of FTIR spectra also supports the reaction scheme, because a hydroxyl peak was observed in conjunction with a slight shift in the characteristic peak of secondary alcohol.

The tensile strength and modulus for such obtained blends are consistent with those obtained by the addition of SMA to the blends of P10EVAOH. The tensile properties of elongation and toughness, however, show a slight decrease. The presence of reactions between EVAOH and SMA is confirmed from the data of the blend with SMA14, which exhibits slower decrease compared to the blend with SMA7. The morphology from the Charpy impact-fractured surfaces reveals that pores and phase coarsening might be the cause for the lower mechanical properties. These countered the effects of reactive compatibilization on the net reduction of tensile toughness. The unstable morphology, not seen for the blends P10E265 with addition of SMA, could be due to the existence of octanol-1 in the EVAOH, which was not
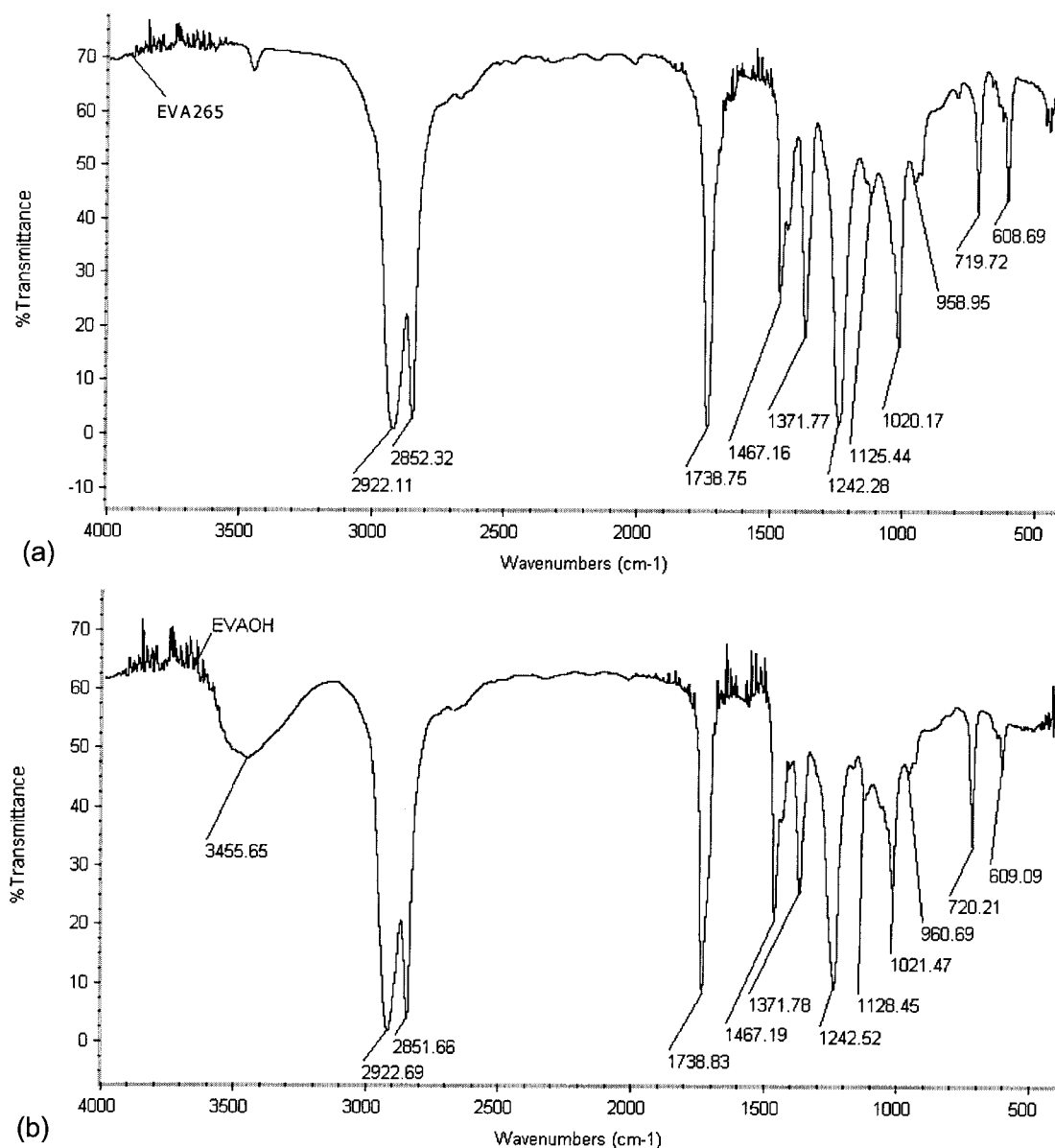
Figure 8 FTIR spectra of (a) EVA265 and (b) EVAOH.

completely removed after the synthesis. The octanol-1 might have reacted with the SMA during processing and caused instability to the morphology.

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