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Intermolecular interactions in polystyrene ionomers/poly(ethylene-*co*-vinyl acetate) blends

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Summary

Specific interactions in blends of salts of sulfonated polystyrene and poly(ethylene-co-vinyl acetate) (EVA) were studied as a function of the blend composition, metal cation (H^+, Na^+, Zn^{2+}) and sulfonate content. Intermolecular association between zinc sulfonate polystyrene (ZnSPS) and EVA in solution was evidenced by increase in the reduced viscosity of the blend relative to that of the pure EVA. Interactions in the solid state were observed in terms of a shift to lower frequencies in the in-plane stretching vibration of benzenesulfonate. Analysis by infrared spectroscopy indicated that the EVA solvated the Zn^{2+} decreasing the ionic associations in the blends. This effect increases when the ion content of ZnSPS increases and led to improvement in the dispersion of the polymeric phases as compared with that in the sodium sulfonate-PS/EVA, sulfonic acid-PS/EVA and PS/EVA blends.

Introduction

As is well known, most polymer pairs are not miscible. However, if specific interactions are present, such as hydrogen bonding (1, 2), ion-dipole (3,4,5) or acid-base interactions (6) and transition metal complexation (7,8,9,10), polymer pairs may be compatible.

Ionomers are a distinct class of polymers containing relatively few ionic groups on a polymer chain (11). They have been used frequently to introduce specific interactions in immiscible blend systems. Lightly sulfonated polystyrene (PS) has been used to promote total or partial miscibility between PS and polar polymers. For example, a poly(styrene-co-styrene sulfonic acid) was compatibilized with poly(ethyl acrylate-co-vinylpyridine) and polyurethane via proton transfer (12). Ion-dipole interactions were responsible for the miscibility of sodium salts of lightly sulfonated polystyrene and poly(ethylene oxide) (5). In blends of zinc salts of sulfonated polystyrene with Nylon-6 and poly(styrene-co-vinylpyridine), the miscibility enhancement was due to formation of interpolymer complexes (7,8). Fourier-transform infrared (FTIR) spectroscopy has often been used to detect the specific interactions in the blends and to clarify the nature of these interactions (2,7,13,14,15).

In this work, we investigated the possibility of improving the miscibility of EVA in PS by introducing zinc sulfonate and sodium sulfonate groups onto PS. The interactions between ZnSPS and EVA in xylene-methanol solution were investigated by viscosity measurements. FTIR spectroscopy was used to obtain information about the nature of the interactions in the blends as well as about the ionic associations within PS ionomers.

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These interactions were examined as a function of the sulfonate content (2.3, 4.0, 4.7, 7.2 mol %), metal cation (H^+, Na^+, Zn^{2+}) and blend composition. The blend morphology was examined by optical microscopy.

Experimental

Materials

Lightly sulfonated polystyrene (HSPS) was prepared from a commercial polystyrene ($\overline{Mv}$ = 350,000) provided by EDN-Camaçari. Sulfonation reactions were carried out in 1,2-dichloroethane at 50°C using acetyl sulfate as the sulfonating agent (16). The zinc (ZnSPS) and sodium (NaSPS) salts were prepared by neutralizing the HSPS in xylene/methanol (90/10 by volume) with a 20% excess of zinc acetate and sodium hydroxide in methanol. The ZnSPS and NaSPS were precipitated with ethanol, filtered, washed several times with methanol, and dried under vacuum at room temperature for 24 hrs and at 60°C for 72 hrs. The sulfonation level (SL) was determined by titration of HSPS in xylene/methanol solution to a phenolphthalein end point using sodium hydroxide in methanol. The sulfonated PS ranged in sulfonate content from 2 to 7 mol % of SO_3H groups. In this nomenclature, sulfonate content of 1 mol % refers to 1 mol of SO_3H groups for every 100 styrenic units. EVA-634 with 28 wt % of vinyl acetate was obtained from Poliolefinas-São Paulo.

Preparation of the blends

The blends were prepared by dissolving both pure polymers in xylene/methanol (90/10 by volume) at a concentration of 1 g/dL. The solutions (volume = 10 mL) were cast on a petri dish, and the solvents were removed by evaporation in an oven at 60°C for 4 days. The resulting films were either translucent or opaque.

Viscosity measurements

Solutions of the pure and mixed polymers in xylene/methanol (90/10 by volume) were made at a concentration of 0.8 g/dL. The reduced viscosity (η_{red}), also named viscosity number, [defined as $(\eta-\eta_o)/\eta_o c$, where η and η_o are the viscosities of the polymer solutions and the xylene/methanol solution, respectively, and c is the concentration of the polymer in g/dL] was measured with an Ubbelohde viscometer at 30.00 ± 0.05°C.

Blends Characterization

Infrared spectra were obtained on a Jasco II, Model Valor III, Fourier transform infrared spectrometer. A total of 100 scans at a resolution of 1 cm^{-1} were signal averaged. Peak positions can, in principle, be located very precisely ($\cong 0.1\ cm^{-1}$) with this technique. In some cases, multiple determinations were made.

The films of the blends were dyed with iodine vapour at room temperature for 10 min, afterward they were observed by an optical microscope (Nikon). When EVA and PS adsorb the iodine vapour, EVA becomes orange and PS pink. In this way, it is possible to identify in the blends the PS-rich phase and the EVA-rich phase. Another tecnique used to identify the components in the polymeric phases was by selective-solvent. The films were imersed in acetone, a nonsolvent to EVA, for 6 hrs at room temperature and further dried under vacuum at room temperature prior to microscopic examination.

Results and Discussion:

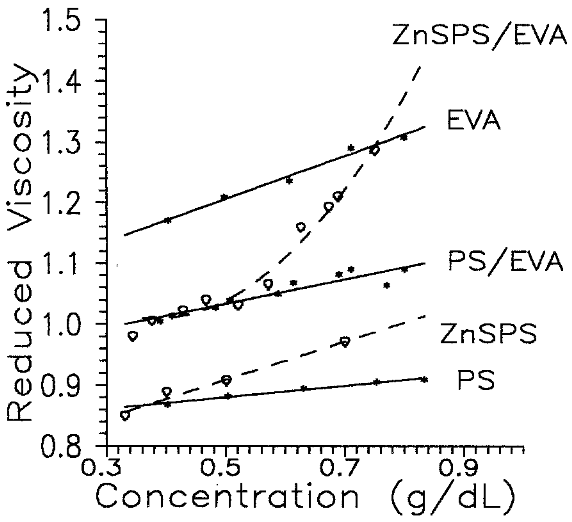


Figure 1:
Reduced viscosity–concentration relations in xylene/methanol

Dilute solution viscosities

Figure 1 displays reduced viscosity-concentration profiles for ZnSPS (SL=2.3 mol %) in xylene/methanol. It shows a reduced viscosity behaviour typical of metal sulfonate ionomers in low polarity solvents (5,8,17). Above about 0.4 g/dL, there is an increase in the reduced viscosity relative to that of PS consistent with intermolecular association of the ion pairs (8).

At lower concentrations (not shown), a decrease in the solution viscosity was observed relative to that of the unmodified PS. The same behaviour was observed for the HSPS (SL=2.3 mol %) solution (not shown) in the concentration range between 0.1 and 0.8 g/dL. This can be explained considering that the ions pairs are associated intramolecularly, resulting in a reduction in the polymer coil size. Similar results have been reported for ZnSPS (SL=0.5 mol %) (8) and HSPS (SL= 2.5 and 4.2 mol %) (17) ionomers in xylene and THF, respectively.

Reduced viscosity-concentration measurements were also conducted on 50/50 PS/EVA and ZnSPS/EVA blends (SL=2.3 mol %) (Fig.1). The reduced viscosities of the PS/EVA blend are intermediary among those of pure polymers. The curve for the ZnSPS/EVA blend shows the influence of employing ZnSPS under the same conditions. At concentrations below 0.5 g/dL, the reduced viscosity values for the ZnSPS/EVA blend approach the same values as that obtained for the PS/EVA blend but a pronounced enhancement of the reduced viscosity for the ZnSPS/EVA blend is seen at concentrations above 0.5 g/dL. In fact, the steepness of the curve is such that above 0.75 g/dL the reduced viscosities are higher than that of EVA. Similar results were observed with ZnSPS (SL=0.5 mol %) and poly(styrene-co-4 vinylpyridine) blends (8). This is an evidence of significant association among the two polymers and can be explained as follows: at low concentrations, no interaction occurs between the acetate groups of EVA and the zinc ionomer. Thus, EVA and ZnSPS behave as two individual polymer coils. When the concentration increases the interaction between the zinc sulfonate groups at the surface of the ionomer and the acetate groups of EVA are favoured. This leads to the formation of a virtual network in solution and consequently an increase in the solution viscosity.

FTIR Spectroscopy:

Figure 2 shows the infrared spectra of PS and sulfonated PS (2.3 mol %) in the region from 850 to 1300 cm^{-1} associated with the stretching vibration region of the sulfonate group. Band assignments were based on literature (7). The symmetric stretching vibrations of the S-O bond are very sensitive to the local environment of the sulfonate group. As indicated by Lu and Weiss (7), there are two different local environments of the SO_3^- anion: associated sulfonate groups in ionic clusters or multiplets, and unassociated sulfonate groups in a nonionic matrix. In the first case, the band was observed at ca 1045 cm^{-1}. When the ionic association is disrupted by a polar solvent and the sulfonate groups are unassociated or solvated, the symmetric stretching band of the anion shifts to ca 1034 cm^{-1}. For example, for a fully sulfonated and hydrated HSPS this vibration occurs at 1033 cm^{-1} while for ZnSPS/Nylon-6 blends (7), the associated sulfonate groups absorb at 1045 cm^{-1} and the unassociated, or solvated, ones at 1030 cm^{-1}. The band at 1030 cm^{-1} is a composite absorption composed of the symmetric stretching vibration of the "solvated" anion at ca. 1034 cm^{-1} and the in-plane bending vibration of the benzene ring of PS at ca. 1029 cm^{-1}.

In the PS spectrum, the absorptions at 1028 and 1003 cm^{-1} were due to in-plane bending vibrations of the benzene ring. The absorptions at 1029 and 1007 cm^{-1}, in the HSPS (SL= 2.3 mol %) spectrum, were also due to the in-plane bending vibrations of the benzene ring but both are coupled by the symmetric S-O stretching vibration of the unassociated sulfonate anion. The spectra of the ZnSPS (SL= 2.3 mol %) and NaSPS (not shown) show, besides the absorptions at 1029 and 1012 cm^{-1}, an absorption at 1040 cm^{-1} due to associated sulfonate groups. Thus, we conclude that in the ZnSPS and NaSPS ionomers a part of the ionic groups are aggregated forming the phase-separated ion-rich domains, called clusters. The absorption at 1040 cm^{-1} is completely absent in the spectrum of the HSPS ionomer, so the ionic groups in HSPS are not associated. This result is consistent with SAXS studies by Peiffer and collaborators (18) who found that in HSPS ionomers with sulfonation levels less than 3 mol % there was no formation of clusters.

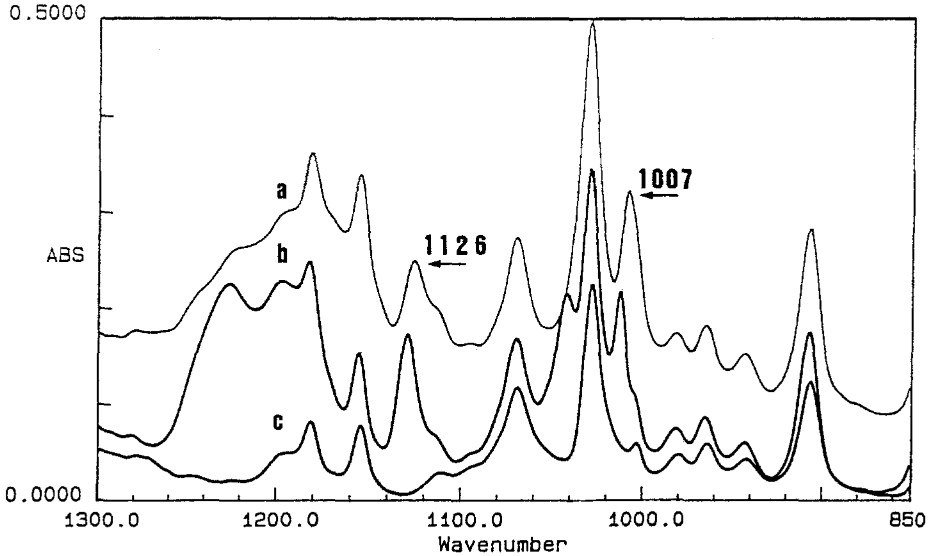


Figure 2: FTIR spectra in the range 1300-850 cm^{-1}. a) HSPS, b) ZnSPS, c) PS. (SL= 2.3 mol %)

Table 1: Frequency of the asymmetric stretching vibration of the benzenesulfonate group as a function of blend composition.

sample (SL=2.3 mol%)	composition (wt %)	frequency (cm^{-1})
ZnSPS	100	1129,0
ZnSPS/EVA	80/20	1127,5
"	50/50	1127,5
"	40/60	1126,8
"	20/80	1125,6
NaSPS	100	1129,0
NaSPS/EVA	50/50	1129,0
HSPS	100	1125,8
HSPS/EVA	50/50	1125,8

Table 2: Frequency of the asymmetric stretching vibration of the benzenesulfonate group as a function of sulfonation level.

sulfonation level (mol %)	ZnSPS/EVA 50/50 (wt%)	NaSPS/EVA 50/50 (wt%)
2.3	1127.5	1129.0
4.0	1126.6	1128.5
4.7	1126.6	1128.5
7.2	1125.5	1128.5

The absorption due to in-plane stretching vibration of the benzenesulfonate groups occurs at 1129 cm^{-1} for the ZnSPS and NaSPS ionomers and at 1126 cm^{-1} for the HSPS ionomer. This vibration is sensitive to the local environments of the sulfonate groups and also shifts to lower frequencies when the sulfonate groups are "solvated" similar to what was observed with the band at 1040 cm^{-1} (7).

Table 1 shows the frequency of in-plane stretching vibration of benzenesulfonate groups for the ZnSPS/EVA blends as a function of blend composition. The vibration shifts to lower frequency with increasing EVA concentration. Similar results have been reported in the literature for ZnSPS/Nylon-6 blends (7). It should be mentioned that the peak shifts reported are small, but they were consistently reproducible in multiple determinations.

The shift to lower frequency can be attributed to intermolecular interactions between the acetate groups of the EVA and either the anion or the cation of the $SO_3^-(Zn^{2+})_{1/2}$. In contrast, for the 50/50 NaSPS/EVA and HSPS/EVA blends, the frequencies of the in-plane stretching vibration of benzenesulfonate were equal to frequencies of the pure NaSPS (1129 cm^{-1}) and HSPS (1126 cm^{-1}), respectively. Therefore, there was no influence of EVA on the benzenesulfonate groups. Together, these results suggest that in the ZnSPS/EVA blends, the EVA interacts with the Zn^{2+}. Absorption frequencies of IR bands are proportional to the force constant, hence a shift to lower frequencies means that the eletrostatic force between the ion pair was weakened by the presence of EVA. This led to weakening of the Zn^{2+} cation's influence on the SO_3^- anion, similar to what was observed when the sulfonated groups in HSPS are fully hydrated (7). This effect, which appeared only in ZnSPS/EVA blends, is indicative of the complex formation between the Zn^{2+} and the acetate group of the EVA.

The influence of the sulfonation level on the interactions in the 50/50 ZnSPS/EVA and NaSPS/EVA blends can be seen in Figure 3. This figure shows the difference spectra in the region of in-plane stretching vibration of benzenesulfonate by subtracting the spectrum of each pure ZnSPS at two sulfonation levels, and NaSPS from the respective blends. As an internal standard, we chose the benzene skeletal ring vibration band at 1601 cm^{-1} because this band is not influenced by environmental effects (14). The absorptions at 1129 and 1040 cm^{-1} for the NaSPS/EVA blend were subtracted and the characteristcs of the resultant difference spectrum is typical for EVA (curve a). In contrast, the difference spectra obtained for the ZnSPS/EVA blends show a reversed peak at 1040 cm^{-1} (curve d) and peaks between 1160 and 1100 cm^{-1} (curves b and d) caused by specific interactions.

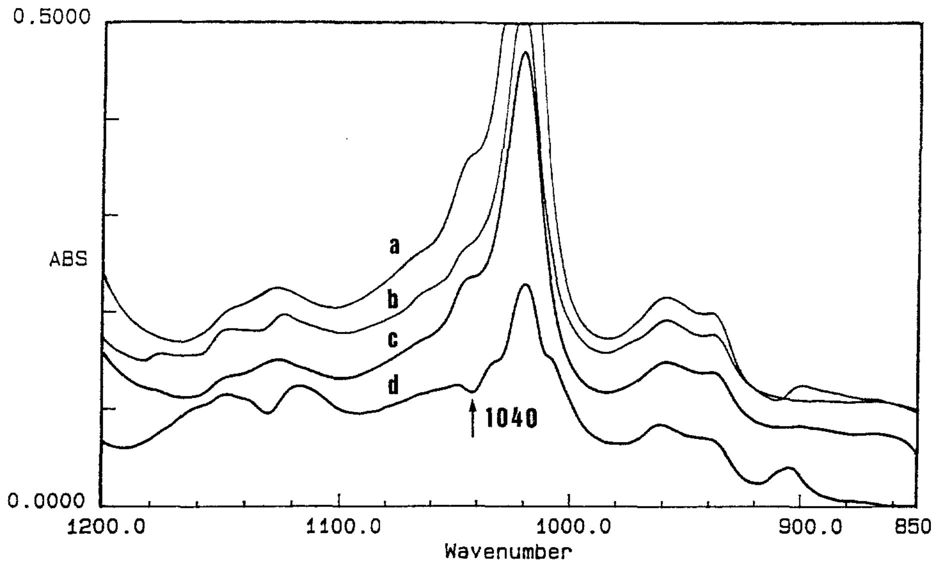


Figure 3: Difference spectra obtained by subtracting the spectrum of each pure ZnSPS and NaSPS from the respective 50/50 blends: a) EVA, b) ZnSPS/EVA (SL=2.3 mol %), c) NaSPS/EVA (2.3 mol %), d) ZnSPS/EVA (7.2 mol %).

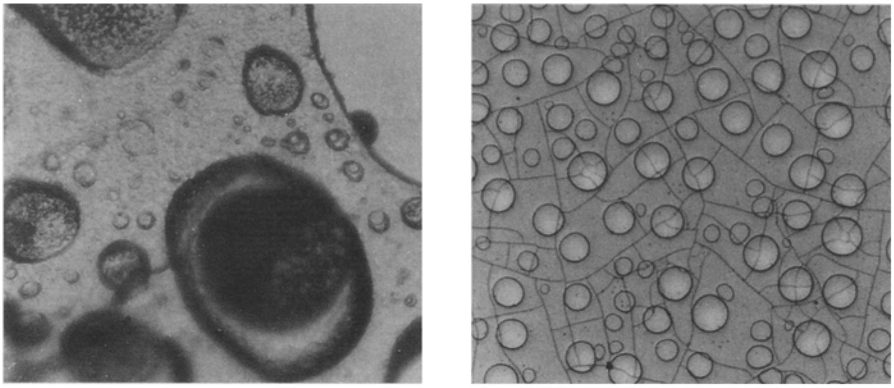
The presence of the reversed peak at 1040 cm^{-1} in the spectrum of ZnSPS/EVA (SL= 7.2 mol %) blend is evidence that there is very little associated SO_3^- groups in this blend. The characteristic shapes of the spectra in the range 1160-1100 cm^{-1} are due to shift of benzenesulfonate band to lower frequency with respect to that of pure ionomer. The shift increases with the sulfonation level (Table 2).

The shift dependence on the sulfonation level is attributed to the increase in the concentration of "unassociated" or "solvated" SO_3^- groups with the increase of the interactions between the acetate groups of EVA and Zn^{2+} of sulfonated PS. For NaSPS/EVA blends no shift was observed (Table 2). So, there was no influence of the acetate groups on the Na^+.

Optical microscopy

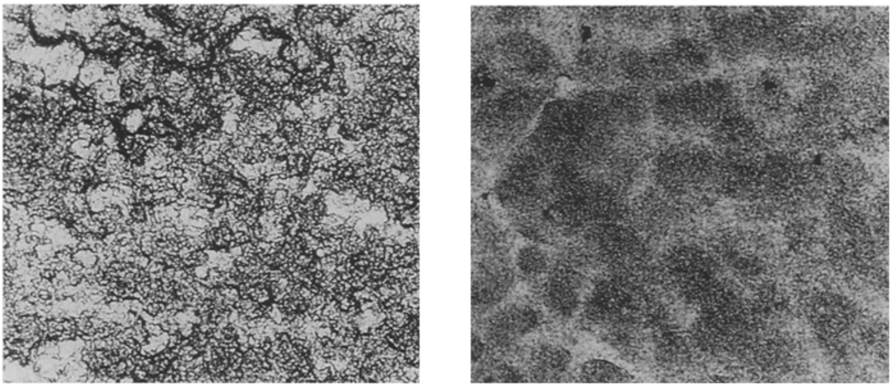
Figure 4a shows a representative photograph of a 50/50 PS/EVA blend which was imersed in acetone. This blend consists of an EVA matrix (lighter areas) in which PS particles (dark areas) are dispersed. The PS particles extracted with acetone leave a hole on the surface of the blend (white area on the right top of the micrograph). The particles appear to be nearly circular. Their average size decreased as the PS content in the blends decreased. Figures 4c and 4d show how the morphology of PS/EVA blend changes as PS is substituted by ZnSPS. The morphology appears to be co-continuous. The PS phase corresponds to the lighter areas in the micrograph. EVA forms the basis of a second co-continuous phase which is darker. The PS domains decreased as the sulfonation level increased.

In HSPS/EVA blend , a significant decrease in the particle size of HSPS is observed as compared to that in the 50/50 PS/EVA blend. This probably was due to an increase in the polarity of HSPS with relation to PS.



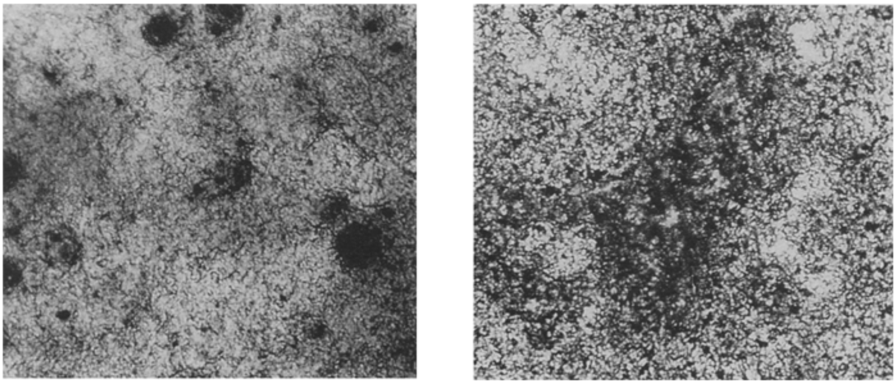
a) PS/EVA

b) HSPS/EVA (SL= 2.3 mol %)



c) ZnSPS/EVA (SL= 2.3 mol %)

d) ZnSPS/EVA (SL= 4.7 mol %)



e) NaSPS/EVA (SL= 2.3 mol %)

f) NaSPS/EVA (SL= 4.7 mol %)

Figure 4: Optical micrographs of the 50/50 blends. a) after imersion in acetone; b), c), d), e), f) dyed with iodine. ____ **100 μm**

The morphology of the 50/50 NaSPS/EVA blends is similar to that of ZnSPS/EVA blends, but the PS phase is larger in the former. The same behaviour was observed for blends with SL= 4.0 and 7.2 mol %. The morphology features of NaSPS/EVA blends may be due to ion-dipole interactions involving unassociated $SO_3^-Na^+$ groups. In ZnSPS/EVA blends, the attractive interactions were more eficient than in NaSPS/EVA blends and can be attributed to Zn^{+2} complexation.

Conclusion

Introduction of sulfonate groups to PS has been demonstrated to influence the dispersion of PS/EVA blends. A significant decrease of the PS domain particle size in the EVA matrix was observed in HSPS/EVA blends. In NaSPS/EVA and ZnSPS/EVA blends the polymeric phases are co-continuous and the improvement in the dispersion of the polymeric phases is as much greater as the sulfonation level is higher in the 2.3-7.2 mol % range. In the first case, this was attributed to ion-dipole interactions. In the ZnSPS/EVA blends, the FTIR analysis shows that EVA solvates the Zn^{2+}. Thus, the improvement in the dispersion may be due to complex formation between Zn^{2+} and the acetate groups of EVA.

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