# Melt/Solution Processable Conducting Polyaniline: Elastomeric Blends with EVA

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**ABSTRACT:** Polyaniline (PANI) protonated with dopant, the sulfonic acid of 3-pentadecylphenoxyacetic acid (SPDPAA; synthesized from an inexpensive naturally existing biomonomer, cardanol), was blended with an elastomeric polymer, the ethylene vinyl acetate (EVA) copolymer. Blending was performed either by emulsion polymerization of aniline into the EVA matrix or by the solution-mixing method. Thin films were prepared by the conventional melt-processing technique for an emulsion-polymerized system and by the solution-casting method for a solution-mixed system. In the case of the emulsion-polymerized system, the percolation threshold occurs at a very low weight percentage of PANI, and a maximum conductivity value of  $0.85 \text{ S cm}^{-1}$  was obtained for 28.5 wt % of PANI. These elastomeric conducting blends were characterized by elemental analysis, FTIR and UV-visible spectral analysis, conductivity measurements, SEM, XRD, tensile properties, TGA, and DSC. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1438–1447, 2002; DOI 10.1002/app.10408

**Key words:** polyaniline; sulfonic acid of 3-pentadecylphenoxyacetic acid; EVA; elastomeric blends

# INTRODUCTION

Electrically conducting polyaniline (PANI) has attracted considerable interest because it is unique among conducting polymers in that its electrical properties can be reversibly controlled both by changing the oxidation state of the main chain and by protonation of imine nitrogen atoms.<sup>1</sup> The wide range of associated electrical, electrochemical, and optical properties, coupled with excellent stability, makes PANI potentially attractive for use as an electronic material in a wide range of applications such as EMI shielding, electrostatic dissipation, light-emitting diodes,<sup>2</sup> photonics,<sup>3</sup> and chemical and biochemical sensors.<sup>4</sup> However,

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these polymers are infusible and intractable and the poor processability hinders their commercialization. So, during the last decade, several research efforts have been made to make PANI processable. One of the strategies employed in this area is to protonate PANI with functionalized protonic acids which induce solution<sup>5</sup> and melt processability $^{6-8}$  to PANI. The second widely adopted strategy is to blend PANI with conventional polymers, because there is an increasing demand for polymeric materials that can be processed using conventional melt-processing techniques.<sup>9</sup> The resulting blends will have attractive mechanical and other properties in addition to the electrical conductivity that can be tailored for various applications.<sup>9</sup>

Conducting blend systems were early made by embedding an inert polymer matrix with conducting fillers (metallic powders, carbon black, etc.).<sup>10</sup> There have been reports on the blending of PANI

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through electrochemical,<sup>11</sup> chemical,<sup>12</sup> and emulsion<sup>13-16</sup> polymerization of aniline (AN) onto polymer substrates. Blends were also prepared by the blending of soluble or processable conducting polymers with insulating polymers in solution<sup>1,5</sup> or in melts.<sup>8,17</sup> Heeger et al.<sup>1,5</sup> and Banerjee and Mandal<sup>18</sup> succeeded in making solution-processed blends of PMMA and a polyaniline-camphor sulfonic acid complex (PANI-CSA) with an extremely low percolation threshold. Reghu et al.<sup>19</sup> reported results on the transport properties of conducting polyblends of PANI-CSA in PMMA. They used *meta*-cresol as a solvent, but, according to Laaska et al.,<sup>20</sup> in the solution-processable systems, the selection of an appropriate solvent is of crucial importance for the electrical conductivity of solution-cast PANI films. For example, PANI protonated with CSA, in selected solvents such as m-cresol, induces extended coil conformation of PANI chains which facilitate polaron delocalization and crystallization of the polymer upon casting.<sup>20</sup> Also, *m*-cresol is suspected to be a cancercausing substance. From the industrial point of view, the fabrication of a thermally processable conducting polymer would be preferable because it is easier and much cheaper. Recently, research at Allied Signal<sup>21</sup> showed that a conductive form of PANI, which was later marketed under the trade name Versicon<sup>TM</sup>, can be dispersed, with the use of added dispersants, in highly polar thermoplastics such as polycaprolactone to give conductive blends having melt processability.

In the case of these conductive blends, a low content of the conducting phase is desirable for applications because an excessive amount may distort other properties of the matrix material such as the mechanical strength or color. Recent studies indicate blends of plasticized PANI and thermoplastic polymers such as PVC with a very low percolation threshold can be made by both solution- and/or melt-processing techniques.<sup>7,22</sup> The incorporation of flexible side chains on the rigid-rod backbone improves the solubility remarkably and lowers the melting or softening points for stiff polymers. The flexible side chains also enhance the miscibility and compatibility of the polymers.

In the case of elastomers, although it is attractive to produce melt-processable blends of conducting polymers with rubbery, nonpolar polymers,<sup>23</sup> only limited work has been reported. Zheng et al. reported on polyblends of *N*-alkylated PANI with the elastomer, ethylene-*co*-vinyl acetate (EVA), but the conductivity values obtained were low.<sup>24</sup> To synthesize highly conducting PANI blends with elastomeric polymers, we adopted the in situ doping emulsion polymerization of AN onto the polymer matrix, EVA, and compared it with the blend obtained by the solution-mixing method. The protonating agent, sulfonic acid of 3-pentadecylphenoxyacetic acid (SPDPAA; synthesized from an inexpensive naturally existing biomonomer, cardanol), used here has been found to act as a very good plasticizing cum protonating agent for PANI.<sup>25</sup> Our studies on in situ doping emulsion polymerization of AN in the presence of SPDPAA, using xylene as the solvent, gave a protonated PANI complex with high conductivity and high crystallinity.<sup>25</sup> On thermal processing, free-standing flexible films with conductivities as high as  $65 \text{ S cm}^{-1}$  could be prepared. The dopant SPDPAA is characterized by the presence of a long aliphatic hydrophobic flexible *n*-alkyl ( $C_{15}H_{31}$ ) side chain, which makes the doped PANI melt-processable and enchances the solubility of PANI in common solvents.<sup>6,25</sup> In this article, we report on the preparation of elastomeric conducting polyblends, PANI-SPDPAA-EVA, by the emulsion polymerization of AN into the EVA matrix. The blend obtained was then thermally processed to obtain free-standing elastomeric and highly conducting films. It is expected that the use of this dopant might pave the way to solutions of the problems (such as processability, cost, and reliability) in the commercialization of the conducting elastomeric blends:



#### **EXPERIMENTAL**

# Reagents

All chemicals used were purchased from S.D. Fine Chem. Ltd. (Mumbai, India). AN was doubly distilled under a vacuum and stored in a refrigerator. Xylene was of spectroscopic grade. EVA resin (28% of vinyl acetate) of cable-grade Pilene EVA 2806 was purchased from M/s Polyolefins Ltd. (Mumbai).

# **Synthesis**

# Preparation of Polyemeraldine Base

PANI was synthesized chemically according to the method of MacDiarmid et al.<sup>26</sup> The neutral base form of PANI was obtained by dedoping the PANI salt in a 3 wt % ammonia solution for 3 h, followed by washing with acetone and drying in a vacuum for 8 h at 60°C.

# Synthesis of SPDPAA

3-Pentadecylphenoxyacetic acid was prepared by the reaction of 3-pentadecylphenol with monochloroacetic acid in alcohol and aqueous alkali.<sup>27</sup> Sulfonation of 3-pentadecylphenoxyacetic acid was carried out by reaction with 98% of concentrated sulfuric acid at 110-120°C.

# Doping and Preparation of Blends of PANI with EVA

Blends of PANI with EVA were prepared either by the solution-mixing method or by the emulsion polymerization method. Doping of PANI base with SPDPAA was carried out by mechanical mixing prior to the preparation of the blend by solution mixing, whereas doping and blending were achieved in a single step in the case of the emulsion polymerization method.

# Solution Mixing Method

Protonation of PANI base with SPDPAA was carried out by the mechanical mixing of emeraldine base of an inherent viscosity of 1.2 dL  $g^{-1}$  (measured at room temperature in 97% H<sub>2</sub>SO<sub>4</sub>, 0.1 wt %) with SPDPAA in a molar ratio of 0.5 SPDPAA to a polymer repeat unit PhN, using an agate mortar and pestle at room temperature to obtain PANI-SPDPAA. A quantity (2 g) of PANI-SPD-PAA was then placed into 98 g of xylene and treated in an ultrasonic bath. The PANI-SPD-PAA complex dissolved to give a viscous deep green solution. A PANI-SPDPAA-EVA polyblend solution was prepared by mixing PANI-SPDPAA into a 10 wt % solution of EVA in xylene at different compositions. Thin films were prepared by solution-casting techniques.

# **Emulsion Polymerization Method**

In a typical polymerization, 9.3 g EVA was dissolved in 300 mL xylene with stirring followed by adding 9.3 g of AN dropwise. Then, a 200 mL xylene solution of 66.5 g of SPDPAA was added slowly. The polymerization was initiated by a dropwise addition of a 50 mL aqueous solution of  $(NH_4)_2S_2O_8$  (11.4 g) into the solution with stirring at room temperature for 12 h. After polymerization, the emulsion of PANI–SPDPAA–EVA was precipitated by pouring into acetone. The dark green sediment was filtered and washed with acetone and water, then vacuum-dried for 48 h. The composites were pressed to thin flexible elastic films at 120°C for 5 min.

# Methods

The FTIR spectra were recorded on a Nicolet IM-PACT 400 D spectrophotometer. The UV-visible spectra were taken in a Shimadzu UV-2100 spectrophotometer. Conductivity was measured by the four-probe method. The XRD pattern was recorded on a Rigaku Geiger-Flex D/MAX series using  $CuK\alpha$  radiation. SEM pictures were recorded using a JEOL JSM-5600LV scanning electron microscope. TG thermograms were recorded on a DuPont thermogravimetric analyzer 951 attached to Thermal Analyst 200. DSC thermograms were taken on a differential scanning calorimeter 2010 attached to a Thermal Analyst 2100. Mechanical properties were determined on an Instron Series IX, Automated Materials Testing System 1.09.

# **RESULTS AND DISCUSSION**

The emulsion polymerization route was adopted for the synthesis of blends of PANI–SPDPAA and EVA, because the effect of unfavored entropic changes of mixing can be overcome if the components of the mixture can coprecipitate. This coprecipitation causes the molecules of the two components to pack together, locking them at a molecular level. We believe that this type of unified ordering of two different polymers leads to polymer–polymer miscibility at the molecular level.<sup>25</sup> Emulsion polymerization provides the optimum conditions for inducing such mixing of both PANI and EVA.

It was found that by keeping the ratio of AN to oxidant and AN to dopant constant, and by varying the AN/EVA ratio, blends with variable nitrogen contents can be obtained. Table I represents the PANI content and the PANI yield in the emulsion polymerization of AN in the EVA matrix with

PANI Content <sup>a</sup> of the Blend (wt %)	Yield of PANI (%)
4 51	50
7.18	43.1
13.56	40.5
18.51	41.625
21.77	43.54
28.5	43.36
	PANI Content <sup>a</sup> of the Blend (wt %) 4.51 7.18 13.56 18.51 21.77 28.5

Table IEffect of EVA on the Polymerizationof AN

 $\begin{array}{l} Polymerization \ conditions: \ (NH_4)_2S_2O_8 \ /AN \ (molar \ ratio) \\ = \ 0.5; \ SPDPAA/AN \ (molar \ ratio) = \ 1.5; \ (AN) = \ 0.2 \ mol \ L^{-1}. \end{array}$ 

<sup>a</sup> Calculated on the basis of elemental analysis, without considering the doping of PANI.

different AN/EVA feeding ratios. The PANI content of the blend was estimated from the elemental analysis of nitrogen. The PANI yield increased when the feeding weight ratio of AN/EVA (wt/wt) decreased. The presence of EVA increases the PANI yield because the presence of bulky groups increases the chain separation between adjacent PANI chains and, consequently, decreases the interchain interactions. Also, the presence of EVA helps the uniform distribution of PANI–SPDPAA in the emulsion particles.

#### **FTIR Analysis**

Figure 1 shows FTIR spectra of the emulsionpolymerized blends of the PANI-SPDPAA-EVA system with different weight percentages of PANI in comparison to the spectrum of EVA itself. It was shown earlier that the band at  $1600 \text{ cm}^{-1}$ , assigned to Q=N-B, B-NH-B (where Q is a quinoid ring and B is a benzenoid ring),<sup>28,29</sup> shifts upon protonation of PANI with SPDPAA to 1128  $cm^{-1}$ .<sup>6,7,25</sup> This is considered to be characteristic of the protonated state. In the present case, for a blend containing 28.5 wt % of PANI, a band at  $1135 \text{ cm}^{-1}$ , diagnostic of the protonated state of PANI, can be clearly observed. Also, it was noted that the protonated PANI peaks became dominant as the PANI content in EVA increased. Similarly, on protonation of PANI with SPDPAA, the bands corresponding to guinoid (N=Q=N), 1593  $cm^{-1}$ , and benzenoid (N—B—N), 1506  $cm^{-1}$ , ringstretching modes of polyemeraldine base are shifted toward lower frequencies, 1560 and 1480  $cm^{-1}$ , respectively.<sup>6,7,25</sup> In the case of the blend of the PANI-SPDPAA-EVA system, having 28.5 wt % of PANI, the band corresponding to the quinoid

(N=Q=N) ring-stretching mode of protonated PANI is found at 1553 cm<sup>-1</sup>. On the other hand, the benzenoid (N-B-N) ring-stretching mode of protonated PANI, usually observed at 1480 cm<sup>-1</sup>, could not be clearly identified due to interference from the EVA peak at 1460 cm<sup>-1</sup>. The band at 3440 cm<sup>-1</sup> (the N-H stretching band of PANI) can be seen in all the spectra except for EVA, and



Figure 1 IR spectrum of (a) EVA and emulsion-polymerized PANI–SPDPAA–EVA with (b) 4.51, (c) 13.5, and (d) 28.5 wt % of PANI.



**Figure 2** UV-visible spectra of solution-mixed PANI–SPDPAA–EVA blend with (a) 10, (b) 15, (c) 20, (d) 25, (e) 30, and (f) 40 wt % of PANI.

with increase in the PANI content, this peak becomes dominant. Similar results were also obtained with the solution-blended samples.

#### **UV-visible Spectral Analysis**

Figure 2 gives the UV-visible absorption spectra of the solution-mixed PANI–SPDPAA–EVA polyblend system. Spectra were measured for blends with different compositions of PANI content. It was observed that, with increase in the PANI content, the absorption characteristics of the protonated state became more predominant. On protonation, the color of the solution changed from blue to green. The two major absorptions around 400 nm (related to the  $\pi$ – $\pi$ \* transition on the polymer chain<sup>30</sup>) and the absorption around 800– 900 nm (ascribed to polaron after doping and corresponding to localization of electrons<sup>31</sup>), characteristic of the protonated state, appeared as the content of PANI increased in the blend.

# **Conductivity Studies**

Figure 3 gives conductivity values against the PANI weight percent in the blends prepared both by the solution-casting and the emulsion polymerization methods. In the solution-mixed blend of PANI–SPDPAA–EVA, the percolation threshold occurred at 10 wt % of PANI,  $(5 \times 10^{-8} \text{ S cm}^{-1})$ . In the case of the emulsion-polymerized system, a melt-processable film having 4.51 wt % of PANI with a conductivity of  $2 \times 10^{-5} \text{ S cm}^{-1}$  was obtained. These values can be compared to those (13

and 5.6 S cm<sup>-1</sup>, respectively) of PANI-SPDPAA (1:0.5 molar ratio) film obtained by the solutioncasting method (xylene) and PANI-SPDPAA synthesized by the *in situ* doping emulsion polymerization method.<sup>25</sup> The observed high value of conductivity for the PANI-SPDPAA (1:0.5 molar ratio) film obtained by the solution-casting method could be due that the polar moieties of the dopant interact more strongly with the less polar xylene and this might lead to the change in molecular conformation from a "compact coil" to an "expanded coil," like the structure for PANI-SP-DPAA in xylene. In the case of the PANI–SPD-PAA-EVA polyblend, the comparatively better value for the emulsion-polymerized system could possibly be due to the better polymer (PANI)dopant interactions obtained with the in situ polymerization of AN in the presence of EVA and SPDAA. In the case of emulsion polymerization, as the content of PANI increased from 4.5 to 28.5 wt %, the conductivity increases to 0.89 S cm<sup>-1</sup>, but for the solution-mixed blend, the conductivity increased to only 0.158 S  $cm^{-1}$  for 40 wt % PANI content. The occurrence of the low percolation threshold limit could possibly be due to the plasticization effect of the long alkyl side chain present in the sulfonated dopant.

Evidence of Mott's variable range hopping conduction in three dimensions has been reported in the literature on PANI blend systems.<sup>32</sup> There are also reports of protonated PANI exhibiting Mott's law in one dimension.<sup>33</sup> Figure 4 represents a plot of ln of normalized resistance versus  $T^{-1/2}$  for a polyblend film of PANI–SPDPAA–EVA (28.5 wt % of PANI) synthesized by the emulsion



**Figure 3** Conductivity versus weight percent of PANI in (a) emulsion-polymerized melt-processable PANI– SPDPAA–EVA film and (b) solution-mixed PANI–SPD-PAA–EVA films.



**Figure 4** Plot of ln resistance versus  $T^{-1/2}$  of PANI–SPDPAA–EVA blend (28.5 wt % of PANI) by the emulsion polymerization route. The normalized resistance–temperature plot is shown in the inset.

polymerization route. It shows that the ln of normalized resistance is proportional to  $T^{-1/2}$  in the temperature range of 35-300 K, indicating a onedimensional variable range hopping conduction. Normalized resistance measured in the temperature range of 50-300 K is shown in the inset of Figure 3. The data are analyzed for Mott's variable range hopping conduction in one dimension in this temperature range, where the nonlinear temperature dependence of thermoelectric power indicates that these samples are far into the insulating regime, well away from the M-I transition. The resistivity increases by several orders of magnitude as the temperature is lowered, indicating the presence of extensive disorder and the formation of inhomogeneous metallic islands as reported earlier.<sup>34</sup> In this case, there is the possibility of formation of aggregates of PANI because of the emulsion polymerization route and that could be the reason for the deviation from metalliclike behavior.

#### Crystallinity and Morphology

Figure 5 shows SEM photographs of the EVA film and both the solution-mixed (20 wt % of PANI content) and emulsion-polymerized (18.51 wt% of PANI content) PANI–SPDPAA–EVA films. In the case of the emulsion-polymerized blend, the sample shows a heavily swollen nature with the presence of some microvoids. The presence of these microvoids is due to PANI aggregates, but in the case of the solution-mixed sample, such voids are not present.

Figure 6 represents the XRD patterns of polyblends of PANI-SPDPAA-EVA with different PANI content. The emulsion-polymerized samples, with different weight percentages of PANI, indicate that for low percentage PANI contents the blends exhibit the same XRD pattern as that of EVA, whereas for the sample with 28.5 wt % of PANI content, the protonated PANI peaks become dominant and it exhibits the same crystalline nature of protonated PANI as that of the PANI-SPDPAA synthesized by the *in situ* doping emulsion polymerization route.<sup>25</sup> The solutionmixed blend system (30 wt % of PANI) also exhibits the peaks characteristic of the protonated PANI. The crystalline nature of PANI, observed in the case of the emulsion-polymerized sample, is due to the more homogeneous protonation of PANI achieved through the emulsion polymerization route, its homogeneous distribution through the EVA matrix, and also the self-assembly of PANI molecules into aggregates.



**Figure 5** SEM photographs (a) pure EVA film, (b) solution-mixed blend film with 20 wt % of PANI, (c) emulsion-polymerized PANI–SPDPAA–EVA blend with (18.5 wt % of PANI), and (d) emulsion-polymerized PANI–SPDPAA–EVA blend film.

#### **Mechanical Properties**

Figure 7 gives the variation of tensile strength with the PANI content of the polyblend films of both the solution-mixed and emulsion-polymerized samples. The tensile strength of polyblend samples decreases with the PANI content in both the solution-mixed and emulsion-polymerized cases. This decrease in tensile strength with increase in the PANI content of the PANI-SPD-PAA-EVA blend could be because PANI might interfere with the intermolecular interactions of the EVA polymer chains: It is possible that PANI might be functioning as a defect in the EVA matrix. The uniform dispersion of PANI in the matrix of EVA, in the case of the emulsion-polymerized sample, might also adversely affect the intermolecular interactions of the EVA polymer chains, resulting in the reduction of tensile properties. Thus, in the case of solution-cast films, the decrease of tensile strength with increase of PANI content is comparatively lower than that of the emulsion-polymerized blend. The emulsion-polymerized blend, with  $\sim 28.5$  wt % of PANI, exhibits a tensile strength of 3.7 MPa, whereas the solution-mixed blend, with a similar weight percent of PANI content, exhibits a tensile strength of 4.5 MPa. It can be seen from the SEM picture that

microvoids are present in the emulsion-polymerized PANI–SPDPAA–EVA blend. The presence of the microvoids might also affect the tensile properties adversely.

Figure 8 represents the percent elongation at break against the PANI content of the polyblend films of both the solution-mixed and emulsionpolymerized samples. In both polyblend systems, the percent elongation decreases with increasing PANI content because PANI is comparatively rigid. The decrease is much lower for the emulsion-polymerized sample where there is homogeneous dispersion of PANI particles.

# **Thermal Studies**

Figure 9(a) represents the TG thermograms of emulsion-polymerized systems and Figure 9(b) represents the TG thermograms of solutionmixed blend systems PANI–SPDPAA–EVA with different PANI contents. Pure EVA itself is thermally stable to 300°C. After 300°C, a double-stage decomposition takes place, first a 20% decomposition from 325 to 400°C, due to the liberation of acetic acid,<sup>35</sup> and the second-stage decomposition, due to the decomposition of the ethylene backbone from 450°C onward. We earlier reported on the



**Figure 6** XRD patterns of (a) pure EVA and emulsion-polymerized PANI-SPDPAA-EVA blend with (b) 4.51 wt, (c) 13.56, (d) 18.5, and (e) 28.51 wt % of PANI and (f) solution-mixed blend with 30 wt% of PANI

decomposition pattern of PANI–SPDPAA alone.<sup>36</sup> The weight losses below 150°C are attributed to the loss of water, oligomers, etc., and those between 250 and 300°C are proportional to their dopant weight percent and are attributed mainly to dopant loss.<sup>36</sup> For the PANI–SPDPAA–EVA polyblend, a two-stage decomposition is observed, in general, for both the emulsion-polymerized and solution-mixed systems, particularly at a lower PANI content. For PANI content less than 11.42%, the behavior of emulsion-polymerized PANI–SPDPAA–EVA is almost the same as that of pure EVA, that is, a two-stage decomposition behavior is observed. But when the PANI content is above 11.42%, the system does not exhibit a



**Figure 7** Tensile strength versus PANI content of PANI–SPDPAA–EVA blend films of (a) emulsion-polymerized and (b) solution-mixed systems.

clear two-stage decomposition after 300°C. It is a multiple-stage decomposition and might involve the decomposition of the dopant, liberation of acetic acid, and decompositions of PANI and the ethylene backbone. The present data indicate that the overall thermal stability of the PANI–SPD-PAA–EVA blend results in a 5% weight loss at 250°C.

Figure 10 provides DSC thermograms of the emulsion-polymerized PANI–SPDPAA–EVA system with different weight percentages of PANI compared with the DSC of pure EVA. As represented in Figure 10, pure EVA has a bimodal melting transition, identified as  $T_1$  (52°C) and  $T_2$  (75°C), in the first heating scans. Okui and Kawai et al.<sup>37</sup> proposed that these two transitions are related to two types of crystals formed in the copolymers with different contents of vinyl ace-



**Figure 8** Percentage of elongation versus PANI content of PANI–SPDPAA–EVA blend films of (a) emulsion-polymerized and (b) solution-mixed systems.



**Figure 9** (a) TG thermograms of (a) EVA and emulsion-polymerized PANI–SPDPAA–EVA with (b) 4.51, (c) 13.5, (d) 21.77, and (e) 28.5 wt % of PANI. (b) TG thermograms of (a) EVA and solution-mixed PANI–SPDPA–EVA with (b) 10, (c) 15, and (d) 25 wt % of PANI.

tate. The lower-temperature transition is assigned to the fringe micellar crystals, and the higher, to the more stable chain-folded crystals. The effect on both the transitions of doped PANI on EVA can be seen. The transition temperature at 52°C undergoes only a slight depression on addition of PANI (this is not observed for the sample having the highest PANI content). The depression observed for curves (b) and (c) might be due to the plasticizing effect of the dopant SPDPA.<sup>6,7</sup> The second transition temperature, observed at 75°C, becomes more prominent and appears at a higher temperature, possibly indicating increasing crystalline order. However, the intensity of these transitions becomes reduced on increasing the PANI content. Figure 10 also shows low enthalpy endotherms, normally observed around 100°C and below 170°C, attributed to the loss of water and oligomers in the case of the thermograms with higher PANI content.<sup>37</sup> The broad exothermic peak, commonly observed for the crosslinking of PANI, can also be observed at a higher PANI content.<sup>36</sup> It, therefore, appears that the PANI content influences the DSC patterns of EVA only at low percentages of PANI, whereas the thermal properties of protonated PANI become dominant with the sample containing 28.5 wt % of PANI.

The blends of PANI with elastomeric polymers are expected to have a number of applications in the cable industry, in electrostatic dissipation (ESD), static discharge, and electromagnetic interference shielding (EMI), and in other areas. Because of the high surface-to-volume ratio resulting from the dispersed network structure of the conducting phase, it is expected that the blend of doped (with SPDPAA) PANI with EVA will have potential for many applications.

#### CONCLUSIONS

Conducting polyblends of PANI–SPDPAA–EVA, prepared by the emulsion polymerization of AN into the EVA matrix, had uniform morphology as demonstrated by SEM analysis. The percolation threshold occurred at very low weight percentage of PANI and a maximum conductivity value of  $0.85 \text{ S cm}^{-1}$  was obtained for 28.5 wt % of PANI.



**Figure 10** DSC thermograms of (a) EVA and emulsion-polymerized PANI-SPDPAA-EVA with (b) 7.18, (c) 18.5, and (d) 28.5 wt % of PANI.

The occurrence of the low percolation threshold limit is explained on the basis of the plasticization effect of the long alkyl side chain present in the sulfonated dopant. Because of the high surfaceto-volume ratio, resulting from the dispersed network structure of the conducting phase, these blends may have many potential applications.

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