Systematic Evaluation of the Preparation of Conducting PANI/ABS Blends

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ABSTRACT: Films of blended poly(acrylonitrile-butadiene-styrene) (ABS) and polyaniline (PANI) were produced by codissolving both components in a common organic solvent, which was then evaporated. The influence of the preparation conditions on the properties of the blends was analyzed by factorial design. The factors evaluated were the PANI content in the blend, the *m*-cresol to chloroform solvent ratio, the dopant used (dodecylbenzenesulfonic acid (DBSA) or camphor sulfonic acid) and its concentration, and the acrylonitrile content in the ABS. The responses analyzed were the flexibility and electrical conductivity of the blends. The results showed that the PANI content in the blend and the acrylonitrile content in the ABS were the major factors influencing both of the assessed responses. The dopant affected only the conductivity, DBSA being preferred for the development of more conductive PANI/ABS blends. The solvent ratio did not have any influence, owing to the uniform expanded coil conformation expected for PANI molecules at the studios ratios. After the best conditions had been established, a percolation threshold study was performed that pointed to a low threshold of 3 wt % PANI necessary in the blend, giving a flexible blend with a conductivity of 3 S/cm. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 825–831, 2010

Key words: conducting polymers; PANI; thermoplastics; ABS; blending

INTRODUCTION

Intrinsically conducting polymers (ICP) have attracted great attention since their discovery[1] due to their potential applications in different devices, such as, batteries,[2,3] electronic tongues,[4] electrochromic devices,[5,6] antistatic devices,[7] sensors,[8–10] and light emitting diodes.[11–13] Among the various known ICPs, polyaniline (PANI) is one of the most promising, as it is simple and economical to make, and has good thermal stability, excellent chemical stability, and relatively high conductivity. The great potential of PANI is, however, minimized by serious disadvantages, such as, insolubility, infusibility, and poor processability,[14] which have hampered the commercial utilization of this polymer. The processability of PANI can be improved by preparing blends of this material with common host polymers that provide good engineering properties.

The specific applications and properties of PANI blends depend on the production method.[15] There

are two main classes of PANI blend production methods: (1) methods based on some kind of synthesis, such as, chemical *in situ* polymerization of aniline,[16,17] electrochemical polymerization of aniline in a matrix covering an electrode,[18,19] or copolymerization of aniline with other monomers resulting in a composite polymer,[20,21] (2) blending methods, such as, dry blending followed by melt processing based on mechanical mixing in an extruder, or hot pressing of PANI with a thermoplastic polymer.[7]

In most studies of conducting blends, the blending process is performed in solution by codissolving both components in a common organic solvent.[22,23] This approach is much used, as it is simple and able to preserve the mechanical and conducting properties of the original compounds. The development of these blends is made possible by counter-ion induced solubilization of the conducting PANI complexes, which can be achieved by doping then PANI emeraldine base (EB) with functionalized protonic acids, such as, camphor sulfonic acid (CSA) and dodecylbenzenesulfonic acid (DBSA).[24]

Several research groups are working with blends of ICPs with common polymers, aiming at technological applications. Various polymers have been studied, such as, polycarbonate,[25,26] poly(methyl methacrylate),[11,27] and poly(styrene-butadiene-styrene).[28,29] In addition, there are in the literature some papers describing the production of blends with PANI and

poly(acrylonitrile-butadiene-styrene) (ABS).[7,23,30,31] The versatility of ABS arises from its composition, which can be changed achieve the best relationship between blend structure and processability. Heeger et al.,[23] in a pioneer study, demonstrated the improved processability of PANI when combined with a suitable functionalized organic acid, such as, CSA. In that study, the PANI-CSA complex was solubilized in m-cresol and mixed with various host insulating polymers, including ABS. According to the authors, this material exhibited low percolation threshold and considerable electrical conductivity. In another study,[7] the PANI-ABS blend was produced by heating in an extruder to a temperature range of 180–190°C. The PANI was doped with a specific ratio of mixed dopants, DBSA and p-toluene sulfonic acid (PTSA). This blend was used to produce electrostatic dissipation charge and electromagnetic interference devices. However, this blending method could degrade the electrical properties of the material. Ahmed[30] obtained enhanced conductivity and low percolation threshold ($\sim$ 4 wt % PANI) when they used picric acid as the dopant for PANI, with ABS in m-cresol solution. In a different work, Dhawan and co-workers[31] prepared a PANI-DBSA-P/ABS composite film, where P is PTSA. The film was used as a sensor material for aqueous ammonia and the composite showed a well-defined response, where the electrical resistance of the composite film was altered by exposure to aqueous ammonia. However, none of these studies dealt with a PANI/ABS system prepared by codissolving both components in a common solvent. Besides, only a few of the experimental variables influencing the conductivity of the final blend were investigated and, even then, a univariate approach was used.

There are a large number of variables that can influence the properties of the blend. For this reason, it would be very useful to conduct a systematic evaluation aimed at establishing the relations between the blending process variables and the characteristics of the blends. In this article, we present an experimental study of the influence of the PANI content, the m-cresol to chloroform rate, the dopant used (DBSA or CSA), the dopant concentration and the acrylonitrile content in ABS on the flexibility and electrical conductivity of PANI-ABS blends. A 2_{IV}^{5-1} fractional factorial design was used for the experimental work. This design is a powerful tool to measure and understand the effects of specific independent variables on the experimental response, with a small number of experiments.[32]

EXPERIMENTAL

Reagents and materials

All reagents used were of analytical grade, unless otherwise specified. All solutions were prepared with deionized and purified water (Resistivity 18M Ω cm^{-1}). Aniline was purified by distillation under reduced pressure before use. The other reagents were used as received. Aniline monomer and $(NH_4)_2S_2O_8$ were supplied by Mallinckrodt. DBSA, CSA, and NH_4OH were obtained from Aldrich and HCl, m-cresol, and chloroform from VETEC.

Polyaniline synthesis

The PANI salt was synthesized by chemical oxidative polymerization of 6.0 mL of aniline in the presence of an inorganic protonic acid, such as, 1.0 mol/L HCl, using 3.756 g of $(NH_4)_2S_2O_8$ as oxidant, at 0°C. The synthesis was carried out for 2 h with continuous stirring. The soluble PANI EB was obtained by dedoping the PANI-HCl salt by stirring with 0.1 mol/L aqueous NH_4OH for 24 h. Finally, the EB was filtered and dried under vacuum for 48 h.

Preparation of PANI/ABS blends

Firstly, PANI EB and ABS were dissolved separately in a mixture of m-cresol and chloroform. These mixtures were stirred for 4 h. Next, the selected dopant was added to the PANI solution, which stirred for 2 h more. Finally, the PANI-dopant and ABS solutions were mixed and stirred for 5 h to obtain the desired blend solution. Films were prepared by casting the blend solutions on glass plates. Solvent was evaporated at 40°C for 24 h, often which the film was detached.

Design of the experiments

A two-level five-factor fractional factorial experiment (2_{IV}^{5-1}), requiring 16 experiments, was designed to evaluate the parameters influencing the PANI/ABS blend properties, conductivity, and flexibility. The five factors tested were: (1) PANI content in the blend, %PANI; (2) m-cresol : chloroform ratio, R; (3) dopant, D; (4) dopant content, DC; and (5) host polymer, HP.

Two levels, high (+) and low (−) were defined for each factor, as shown in Table I. The levels of variable 2 relate to the m-cresol content in the solvent mixture. The levels of variable 4 relate to the molar ratio between dopant and PANI in the blend. The host polymers classified as ABS 1 and ABS 2 are from different suppliers. The ABS 1 was supplied as polymer plates with 23.63% of acrylonitrile and ABS 2 was supplied as a powder with 12.46% of acrylonitrile. Their compositions were estimated after elemental analysis. Table II describes the 16 experiments proposed by the fractional factorial design. These experiments were conducted in a random order. The levels in the variable host polymer

TABLE I
Variables Evaluated in the Preparation of PANI/ABS Blends

Independent variables	Low level (−)	High level (+)
PANI content (%PANI)	5 wt %	20 wt %
m-cresol : $CHCl_3$ ratio (R)	25%	75%
Dopant (D)	DBSA	CSA
Dopant content (DC)	1 : 1	1 : 2
Host polymer (HP)	ABS 1	ABS 2

column in Table II were fixed by the generating function HP = %PANI × R × D × DC.

Characterization

Electrical conductivity of the blends was measured with a Keithley 2400 source meter, using the recommended two-probe method. The measurements were performed on 20-μm thick films. Flexibility was not measured quantitatively. This property was observed qualitatively by subjecting the films to a 90°-fold. The blends were defined as "flexible" if did not crack visible after the folding. On the other hand, even if a little crack was observed, the blend was classified as "brittle." The contrasts related to this response were calculated after giving arbitrary values, such as, 0 to the flexible blends and 1 to the brittle.

RESULTS AND DISCUSSION

The flexibility results and the detailed 2_{IV}^{5-1} fractional factorial design are shown in Table II. The blends prepared under the conditions shown for experiments 2, 8, 12, and 14 were very brittle. The remaining films were flexible. The contrasts obtained for the flexibility response indicate that the factors exhibiting most of the influence over this response are PANI content and host polymer. Their first-order effects and the second-order interaction effect between PANI content and host polymer showed non-null values, whereas all the other calculated effects had null contrasts. The contrast for the first-order effect of the variable PANI content was −0.5, whereas those obtained for the variable host polymer and for the interaction effect between the two variables were both 0.5. The negative signal for %PANI indicates that the increase in the amount of PANI from 5% to 20% in the blend impairs the flexibility of the material, making it more brittle. This is an expected result because PANI has poor mechanical properties.[14] Thus, as the amount is increased, the blend gradually loses its flexibility and mechanical strength.

The positive the contrast for HP shows that ABS 2 tends to produce more flexible blends than the other

ABS tested. The improved flexibility afforded by ABS 2 can be explained in terms of its acrylonitrile content. ABS 2 contains 12.5% of acrylonitrile and ABS 1 23.6%. Although it is known that ABS with a higher proportion of acrylonitrile has better thermal and chemical properties,[32,33] the improvement comes at the cost of poorer processability.[32,33] In the literature, it is reported that blends made with SBS containing higher percentages of acrylonitrile show lower flexibility.[33] This result was confirmed in our observation that the blend produced from ABS with more acrylonitrile was less flexible. One possible explanation for this effect is the formation of hydrogen bonds between the polar groups of PANI and the acrylonitrile in ABS, which could make blends synthesized with ABS 1 to be stiffer than those prepared with ABS 2.

However, the flexibility of the blend is not an exclusive function of the polymer base or the amount of PANI used. The significance of the second-order interaction effect between the two variables is that a flexible blend can also be produced with 20 wt % PANI, as long as ABS 2 is used and with ABS 1, as long as 5 wt % PANI is used. The blend was brittle only when a higher amount of PANI (20 wt %, in our case) coincided with an ABS with a higher content of acrylonitrile (ABS 1, in our case).

The electrical conductivity results for each experiment are summarized in Table II. The conductivity of the blends varied from 0.02 to 9.25 S/cm. First, a normal probability plot of the effects was constructed and is shown in Figure 1. In this figure, all points near the vertical axis (around zero) represent

TABLE II
Fractional Factorial Design Matrix Describing the PANI/ABS Blends Prepared in Each Experiment and Their Observed Flexibility and Conductivity (σ) Experiment

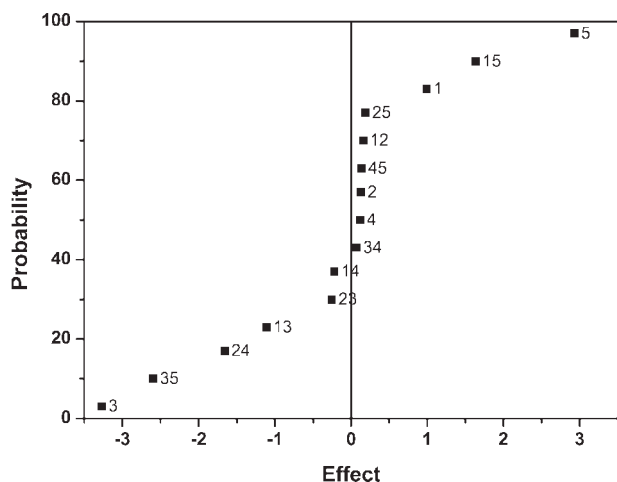| Experiments	Variables					Response	
	%PANI	R	D	QD	HP	Flexibility	σ (S/cm)
1	−	−	−	−	+	F	3.17
2	+	−	−	−	−	B	0.13
3	−	+	−	−	−	F	1.30
4	+	+	−	−	+	F	9.35
5	−	−	+	−	−	F	0.22
6	+	−	+	−	+	F	0.17
7	−	+	+	−	+	F	0.16
8	+	+	+	−	−	B	0.03
9	−	−	+	+	−	F	1.39
10	+	−	−	+	+	F	8.58
11	−	+	−	+	+	F	3.98
12	+	+	−	+	−	B	0.17
13	−	−	+	+	+	F	0.80
14	+	−	+	+	−	B	0.02
15	−	+	+	+	−	F	0.02
16	+	+	+	+	+	F	0.51

F, flexible; B, brittle.

Figure 1 Normal probability plot of the effects related to the evaluation of the conductivity.

effects arising from random error and are considered insignificant to the change in the response. On the other hand, the effects located away from the central line could be regarded as significant to the conductivity, because their variation is not caused by the inherent deviations of the experimental measurements. Consequently, the most important contrasts identified by analyzing Figure 1 are the first-order effects of the variables 1, 3, and 5, and the second-order interaction effects between the variables 13, 15, 35, and 24. The 24 interaction effect actually represents the response of the third-order interaction effect among variables 135, because the variables 2 and 4 had no significant effect on conductivity (as discussed later). Thus, we can conclude that the PANI content, the dopant used and the host polymer used are the main factors defining the blend conductivity.

The positive signal of main effect of variable 1 (%PANI) shows that, as expected, raising the proportion of PANI in the blend leads to an increase in its electrical conductivity. This increase should be linear, according to percolation theory.[34] In this case, although all the blends had an amount of PANI exceeding the percolation threshold, over 3 wt % as we shall see later, a statistically significant increase in conductivity was still caused by increasing the PANI content.

The negative value found for the effect of variable 3 (dopant) shows that conductivity was higher when DBSA was used as dopant. This could be related to a DBSA-induced increase of the solubility of PANI in ABS, because a dopant with a long alkyl chain, such as, DBSA, promotes a larger interaction between the PANI chains and solvent molecules carrying the insulation polymer chain.[7] The preparation of miscible conducting blends results in retention of both electrical and mechanical properties, which may be due to the strong H-bonding between polya-

crylonitrile chains of ABS and the dopant moiety in the presence of solvent, forming a tertiary structure.[35] According to Figure 1, a mean decrease of more than 3 S/cm is observed when CSA is used as dopant. At first glance, it may appear that the effect is negligible. However, if we calculate from Table II the average conductivity for the eight experiments performed with CSA (0.34 S/cm) or DBSA (3.53 S/cm), we perceive that a 10-fold increase in the conductivity is achieved simply by replacing CSA by DBSA.

In the literature, there are many papers describing the influence of CSA on the electrical conductivity of PANI.[24,36] It is well-established that the PANI molecular chain can be isolated in two chirally-distinct helical forms, depending on whether $(+)$ or $(-)$-camphor sulfonic acid is used as the dopant acid. When only one enantiomer is selected for doping, PANI of higher conductivity and more metallic features is produced than when a racemic mixture of camphor sulfonic acid is used producing a mixture of the two optical isomers of the PANI backbone.[37] In the case of the PANI-CSA/ABS blends described here, a mixture of the $(+)$ and $(-)$ forms of CSA was used, impairing the electrical conductivity of the PANI.

The positive signal for the effect of variable 5 (host polymer) indicates that the conductivity by the blends increases by around 3 S/cm when the ABS with lower acrylonitrile content is used. This represents an eightfold increase over the average conductivity of the blends prepared with the ABS containing more acrylonitrile. The interaction of PANI with ABS could be explained by interactions between the nitrogen groups on PANI and the characteristic units of ABS (acrylonitrile, butadiene, and styrene). However, considering all three components, the cyan group of acrylonitrile is clearly the most reactive. It could interact strongly by hydrogen bonding with the nitrogen of PANI, causing the blends to become brittle, as discussed earlier. At this point, one should recall that the conformation of PANI in the blend strongly influences the jumps distance needed for delocalization of the charge-carriers and, as a consequence, the conductivity of the blend, and that the chain conformation of doped PANI is influenced by several factors, such as, chemical nature of the dopant, host polymer, and solvents.[36]

The main effects 2 and 4, related to the *m*-cresol : chloroform solvent ratio and dopant content, respectively, were not significant to the variation of the blend conductivity. In the range of solvent ratios tested in effect 2, the PANI conformation is constant, according to MacDiarmid and Epstein[38] Increasing the *m*-cresol content in the solvent mixture leads to an increase in the reduced viscosity of the solution, as *m*-cresol interacts strongly with the PANI chain, promoting a change of conformation from "compact

TABLE III
Complete 2^3 Factorial Design, Running in Duplicate, Resulting from Exclusion of Variables 2 and 4, Used for to Estimate of the Real Effects Related to Variables 1, 3, and 5

Exp.	Original exp.	1	3	5	σ	σ		Variance
1	1 and 11	−	−	+	3.17	3.98	3.57	0.331
2	2 and 2	+	−	−	0.13	0.17	0.15	0.001
3	3 and 9	−	−	−	1.30	1.39	1.34	0.004
4	4 and 10	+	−	+	9.35	8.58	8.97	0.294
5	5 and 15	−	+	−	0.22	0.02	0.12	0.020
6	6 and 16	+	+	+	0.17	0.51	0.34	0.059
7	7 and 13	−	+	+	0.16	0.80	0.48	0.206
8	8 and 14	+	+	−	0.03	0.03	0.03	0.000

Effects

1	3	5	13	15	35	135
0.99	−3.27	2.93	−1.11	1.64	−2.59	−1.66

coil" to "expanded coil."[38,39] Thus, occurs with a minimum of 20% of *m*-cresol in the solvent mixture. In this study, the minimum percentage of *m*-cresol was 25% and the maximum 75%. Thus, it is not expected that any significant change would be observed in the conformation of PANI. Effect 4, dopant content, also had no influence on the electrical conductivity, which could be related to the amount of added dopant being higher than that of the imine nitrogen atoms, which would be fully protonated by dopant molecules.

Because the effects 2 and 4 were not significant for the response conductivity, the 2_{IV}^{5-1} fractional factorial design could be reduced to a 2^3 full factorial design with the experiments now running in duplicate (eight experiments with one replicate). Given the duplicate tests, it was now possible to estimate the errors associated with the measurements and, consequently, the real significance of the effects. Table III shows the results of average conductivity, variances, and the calculated effects for this new design. The confidence interval estimated for the pure error was ±0.78, for a confidence level of 25%. Thus, the three variables 1, 3, and 5 were confirmed as statistically significant to the variation of the conductivity.

From the responses obtained in the eight experiments (in duplicate) described on the complete factorial design, a functional relationship was established among the independent variables and the response electrical conductivity. The empirical model equation based on statistical analysis of these results is as follows:

$$\sigma = 1.876 + 0.992 \times_{PANI} - 3.266 \times D + 2.928 \times HP$$
$$- 1.106 \times_{PANI} D + 1.634 \times_{PANI} HP$$
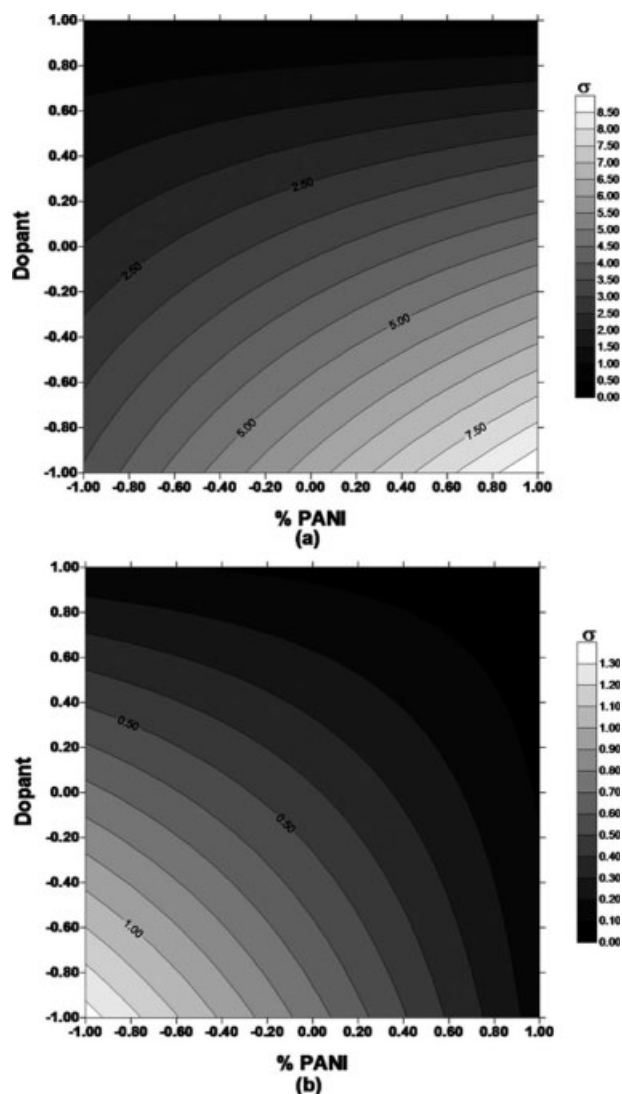$$- 2.594 \times D \times HP - 1.658 \times_{PANI} D \times HP \quad (1)$$

Figure 2 Two-dimensional contour plots relating the dopant used and the PANI content in the blend, obtained from each host polymer utilized: (a) ABS 1 and (b) ABS 2.
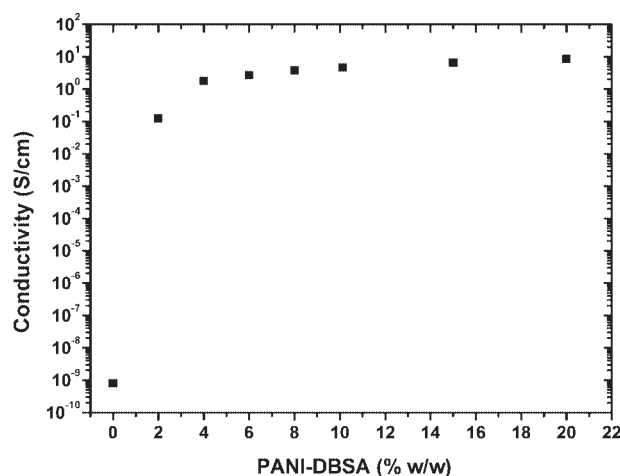
Figure 3 PANI content (wt %) versus conductivity plot showing the low percolation threshold of PANI in the blend.

Analysis of variance (ANOVA) showed that the coefficient of determination (R^2) for this equation was 0.99326, indicating a very good adjustment of the linear model to the experimental data. The F model value, calculated as the ratio of mean square regression to mean square residual, is 189.49, showing the high significance of the model, that is, the present model is a good predictor of the experimental results. A lack-of-fit test was also performed and the results show that the model appears to be adequate for the observed data at 95.0% confidence level.

Figure 2 presents the two-dimensional contour plots calculated using eq. (1) and the two values for the variable host polymer (−1 and 1 for ABS 1 and ABS 2, respectively). Figure 2(a) shows the contour plot for ABS 1 and Figure 2(b), the plot for ABS 2. It is observed that the variable %PANI showed opposite behavior in each plot. The maximum response was obtained when the host polymer with lower acrylonitrile content (ABS 2) was used together with 20 wt % PANI, leading to a conductivity value of 9 S/cm. By contrast, the host polymer with higher acrylonitrile content (ABS 1) reaches a maximum conductivity of 1.3 S/cm at 5 wt % PANI. These results are strictly related to the flexibility response, where the worse results were obtained by using ABS 1 as the host polymer. In other words, increasing the acrylonitrile content in the host polymer impairs blend properties, such as, conductivity and flexibility.

At the end of the study, it was noted that two of five variables were not important for either the flexibility or conductivity of the blends. The other three (%PANI, dopant, and host polymer) were important for at least one of the two measured properties. Among these three variables, two are nonmetric and dichotomous (dopant and host polymer). Thus, to

search for a composition of a PANI/ABS blend that is flexible and uses the minimum necessary amount of PANI to produce a satisfactory conductivity, the PANI percolation threshold was investigated keeping both the dopant agent (DBSA) and the host polymer (ABS 2) constant. The other variables, *m*-cresol : chloroform ratio and dopant content, were kept at their minimum levels to use a smaller amount of reagent (dopant and *m*-cresol). Thus, the PANI content in the blend was increased from 0 to 10 wt %, in steps of 2 wt %, and from 10 to 20 wt %, in steps of 5 wt %. Figure 3 shows a plot of the logarithm of the conductivity against the percentage of PANI showing the percolation threshold to be ∼ 3 wt %, where the conductivity was 3 S/cm. This threshold is similar to that found in the literature for other blends of PANI with common polymers.[15,28,40,41]

CONCLUSIONS

The aim of this article was to present simple procedure to evaluate the best conditions for preparation PANI/ABS blends with desired properties. A fractional factorial experimental design was used to less the influence of several preparation variables over two properties of the blends: flexibility and conductivity. Among the five variables studied, the chemical nature of the dopant, the acrylonitrile content in the ABS, and the PANI content in the blend were the factors that strongly influenced at least one of the measured properties. An increase of the PANI content can be expected to cause an increase in the conductivity of the blend, but also causes a loss of flexibility, especially if an ABS with a high proportion of acrylonitrile is utilized. The chemical nature of the dopant influenced only the conductivity, the blends produced with DBSA showing 10-fold higher conductivity than CSA base ones, on average. The other variables, *m*-cresol : chloroform ratio and dopant content, were not significant and were kept at their minimum levels in a percolation threshold study, using the ABS with lower content of acrylonitrile and DBSA as dopant. A low percolation threshold of 3 wt %, with a conductivity of 3 S/cm, was observed.

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