Simple Chemical Polymerization Method for the Deposition of a Conducting Polyaniline on the Surface of Acrylonitrile–Butadiene–Styrene. II. Treatment in Organic Free Solvent

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ABSTRACT: We developed a simple method for the deposition of a uniform layer of polyaniline (PANI) on the surface of acrylonitrile–butadiene–styrene (ABS). The method consisted of two steps: the soaking of ABS samples in a water-based aniline solution stabilized by surfactants followed by the oxidative polymerization of the adsorbed and absorbed monomer. The three types of surfactants (molecular N,N-dimethyl-octalamine-N-oxide, anionic sodium dodecyl sulfate, and cationic hexadecyl trimethyl ammonium bromide) were used to prepare and stabilize the aniline emulsions in water. After treatment, the ABS surface was completely covered by PANI (as seen with scanning electron microscopy). The surface conductivity after PANI coating reached values between 10^{-3} and 10^{-4} S/□ in the best developed conditions. The chemical nature of the surfactant affected the particular setting of the aniline/surfactant emulsion preparation (time of ultrasonification = 15–30 min), its optimal concentration (2–10 wt % aniline and 0.1–0.2M surfactant), and other parameters of treatment, such as time (10 s to 20 min) and temperature (20–60°C) of soaking. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1752–1758, 2004

Key words: coatings; surfactants; conducting polymers; block copolymers; polybutadiene

INTRODUCTION

The development of a simple method for the surface conductive coating of different polymers has great importance in the field of antistatic coating or EMI (electromagnetic interference) shielding.[1–4] Such a treatment permits the combination of the mechanical properties of insulating polymers with the electrical conductivity of the deposited material. Coating by conducting polymers has been proposed recently (for reviews see refs. 5 and 6), and polyaniline (PANI) has been found to be one of the most promising because of its low cost, high stability, and satisfying electrical properties.[7–10]

In a previous work,[11] we reported a very simple chemical polymerization method for the coating of acrylonitrile–butadiene–styrene (ABS), one of the most commercialized plastics, by PANI. The method was based on permeation of aniline through the ABS matrix. Thus, in the first step of the two-step treatment, the ABS sample was soaked in an aniline/ethyl alcohol solution. The use of an organic solvent permitted us to adjust the concentration of aniline and its absorption by the ABS matrix and to control the quantity of deposited PANI that was produced in the second step of the treatment, oxidative chemical polymerization. The appropriate concentration of aniline in ethanol solution was found to be 5–15 wt %, and the dipping time was 20 to 5 min (for a bigger concentration, a lesser time was used) for the 30°C treatment. In these conditions, the PANI layer was uniform and grew in depth through ABS from 5 to 7 μm; the surface layer was modified and exhibited significant conductivity. As soon as the conductive layer penetrated into the ABS matrix, it was very resistive to mechanical treatment and was stable in ambient conditions.

From a technological point of view, the application of an organic solvent in large-scale production is not very friendly. So, we tried to eliminate ethyl alcohol and replaced it with more neutral substance such as water. Evidently, aniline does not dissolve in water, so we used surfactants and ultrasonification to homogenize the mixture and make it suitable to soak the ABS samples. The results are reported in this article.
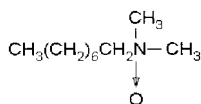
EXPERIMENTAL

Surfactants

The three types of surfactants generally considered are neutral, or molecular; anionic; and cationic, depend-

CH₃(CH₂)₆CH₂N—CH₃ with CH₃ group and O

Scheme 1 *N*,*N*-dimethyl-octalamine-*N*-oxide (dimethyl I) molecular surfactant.

ing on their chemical structure in the dissolved state. We tested all of these. As a molecular surfactant, we used *N*,*N*-dimethyl-octalamine-*N*-oxide (dimethyl I); its molecular structure is presented in Scheme 1. The product was purchased from Fluka Chemie AG (Sigma Aldrich) as a 0.1*M* solution in water and was used as received. As an anionic surfactant, we used sodium dodecyl sulfate (sulfate II), and as a cationic surfactant, we used hexadecyl trimethyl ammonium bromide (bromide III). Their molecular structures are presented in Schemes 2 and 3, correspondingly. They were purchased from Fluka (as salts) and before use were dissolved in water to give 0.1*M* solutions.
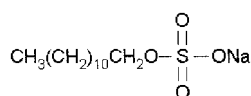
Aniline solutions

For the soaking step of the treatment, 2 and 5 wt % aniline solutions were prepared in a 0.1*M* solution of the corresponding surfactant. The molecular ratios of aniline to surfactant were close to 2:1 and 5:1. Immediately after preparation, none of the three mixtures was miscible and needed 15–25 min of ultrasonication. After that, the homogeneous emulsions of aniline in water were obtained. The emulsions were stable and did not separate into two phases for at least 2 months, the period of time that the prepared solutions were stored.

The 5 wt % concentration of aniline in 0.1*M* of any surfactant seemed to be close to the highest limit of concentration that could be achieved under laboratory ultrasonification. The more concentrated solutions (10 wt %) contained drops of aniline still observable after 1 h of ultrasonification so that the mixtures were not homogeneous enough. Increasing the temperature (to 60°C) and surfactant content (we tried the 0.2*M* sulfate II and bromide III solutions) helped to prepare adequate mixtures, but aniline precipitated under cooling, and the coating results were unsatisfactory: the coverage by PANI was very fast and uncontrollable.

Coating procedure

The two-step method of PANI coating consisted first of soaking the ABS samples in the aniline/surfactant

solution and second of the chemical oxidative polymerization of absorbed aniline to PANI in a 0.5*M* peroxidisulfate ammonium solution in 1.5*M* HCl. The time of polymerization was 10 min, and the experiment was conducted at ambient temperature (~25°C). The samples, before immersion into a second solution, were rinsed in water (without additives) and dried between sheets of filter paper. In the soaking step, we varied the time (30 s to 20 min), the temperature (25–65°C), the concentration of aniline (2 and 5 wt %), and the nature of the surfactant (see Schemes 1–3).

Surface conductivity

Measurements were done by a two-probe method. The two silver contacts were attached to the surface of each sample (the area between them was ~1 cm²) to improve the electrical contact between the polymer and the finely polished Cu wires from the ohmmeter. These settings ensured a stable geometry of the measured area and permitted a direct comparison of the data obtained at different moments after coating (aging properties). The maximum resistance that could be measured by our analyzer was $10^7 \Omega$, corresponded to 10^{-7} S/□, so there was a limit to the evaluation of the surface conductivity of the ABS samples. Samples with this level of conductivity were treated very slightly and were practically colorless.
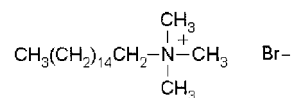
Electron microscopy

Scanning electron micrographs were taken on a JEOL JSM 6300 scanning electron microscope. The samples were coated with carbon before the scanning electron microscopy (SEM) measurements.

RESULTS AND DISCUSSION

Treatment and conductivity

The most complete experiments on the ABS coating by PANI were done with the sulfate II surfactant. In Figure 1, the dependence of surface conductivity on the time of soaking in the aniline/sulfate II solution at 30°C is reported. In the 2 wt % aniline emulsion, coating was not developed at all, samples did not acquire the greenish color of PANI, and the surface conductivity was at the limit of our analyzer (Fig. 1, curve 1). The 5 wt % solution, in contrast, showed

CH₃(CH₂)₁₀CH₂O—S(O)(O)—ONa

Scheme 2 Sodium dodecyl sulfate (sulfate II) anionic surfactant.

CH₃(CH₂)₁₄CH₂—N⁺(CH₃)(CH₃)—CH₃   Br⁻

Scheme 3 Hexadecyl-trimethyl-ammonium bromide (bromide III) cationic surfactant.
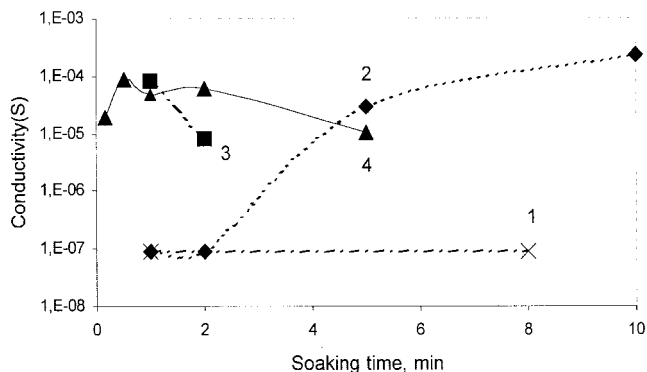
Figure 1 Surface conductivity of ABS samples covered with PANI in the two-step process described in the Experimental section: dependence on soaking time in an aniline solution stabilized with sodium dodecyl sulfate (sulfate II) at room temperature (26°C): (1) 2% aniline/0.1M sulfate II, (2) 5% aniline/0.1M sulfate II, (3) 10% aniline/0.1M sulfate II, and (4) 10% aniline/0.2M sulfate II.

good time-resolved behavior (Fig. 1, curve 2): with short periods of soaking, the coating was insignificant, but a slight green coloration was observed after only 1 min of treatment. After 5 min, the obtained coating was uniformly and deeply green, and after 10 min of soaking, a black coloration and maximum conductivity was achieved.

As mentioned in the Experimental part, the 10 wt % aniline solution in 0.1M sulfate II was not homogeneous enough and contained small drops of aniline. The soaking of ABS samples in such a mixture (Fig. 1, curve 3) for just very short periods of time resulted in a surface PANI coating of poor quality: samples were black with no adhesion of PANI to ABS. The conducting layer can be completely eliminated by simple mechanical treatment. The surface conductivity was high, close to the maximum level. Increasing the sulfate II concentration to 0.2M (Fig. 1, curve 4; molecular ratio of aniline to surfactant = 5:1, the same as the 5 wt % solution with 0.1M sulfate II) and decreasing the time of treatment to 10 s did not help to control the process. Thus, the 10 wt % aniline/sulfate II solution was too concentrated and could not be used for the proposed coating method.

The influence of the chemical nature of the surfactant on PANI coating is shown in Figure 2. The 5 wt % aniline solutions were used for comparison. In contrast to the 5 wt % sulfate II solution (Fig. 2, curve 1), the treatment in the dimethyl I and bromide III mixtures resulted in very deep black coatings at all soaking times (Fig. 2, curves 2 and 3). The resulting PANI films seemed like the 10 wt % sulfate II coating. Nevertheless, the adhesion of PANI was better than in that case, and the samples did not paint the filter paper black. The achieved conductivity was higher at short times of soaking and then decreased to a constant level

well below the limit of conductivity observed for the sulfate II surfactant. The shape of curves 2 and 3 in Fig. 2 was similar to 10 wt % sulfate II coating in Fig. 1, and thus, we concluded that for surfactants I and III, the 5 wt % concentration was too high, so the process was incontrollable.

Like in the previous case, we tried to influence the coating through the variation of the aniline/surfactant ratio. The concentration of bromide III in the 5 wt % aniline solution was increased to 0.2M (the ratio was dropped to 5:2), and after an additional 5 min of ultrasonification, the new coating was performed. The resulting process was more controllable, and a coating with a fine green coloration was obtained after just 2 min of soaking. The conductivity of the samples was less than 10^{-7} S/□ level. Thus, we propose that the additional ruling parameter besides aniline concentration was the molecular ratio between the aniline and surfactant. This finding reflects the importance of aniline drop size in the soaking mixture. Aniline and water are not miscible and should form a fine emulsion stabilized by the surfactant during ultrasonification. The surfactant concentration should determine the radius of a stable sphere (drop) of aniline in such an emulsion. During the soaking of ABS, these drops adhere onto surface, and aniline could be absorbed by a polymer matrix similar to that in the aniline/ethanol mixture.

Another way to control the PANI coating is through temperature during soaking. The corresponding thermal treatment was performed with the 2 wt % aniline solution for each surfactant. At ambient temperature (~25°C), none of these 2 wt % mixtures worked well, and the obtained samples were partially or completely colorless or covered by small irregular patches of a light greenish color. The surface resistance in these cases was higher than the analyzer limit and could not be evaluated. Increasing the temperature permitted us
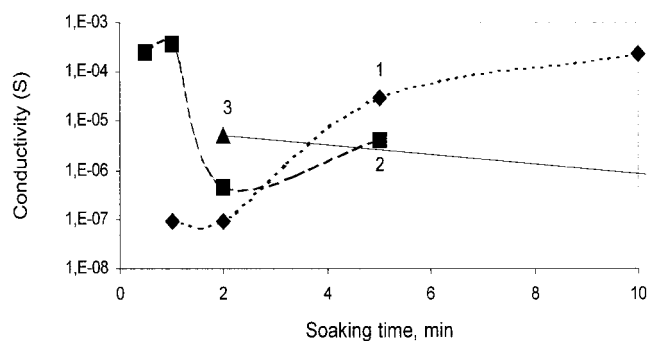

Figure 2 Surface conductivity of ABS samples covered with PANI in the two-step process described in the Experimental section: dependence on soaking time in a 5% aniline solution stabilized with different surfactants (0.1M) at room temperature (26°C): (1) sodium dodecyl sulfate, (2) N,N-dimethyl-octalamine-N-oxide, and (3) hexadecyl-trimethyl-ammonium bromide.
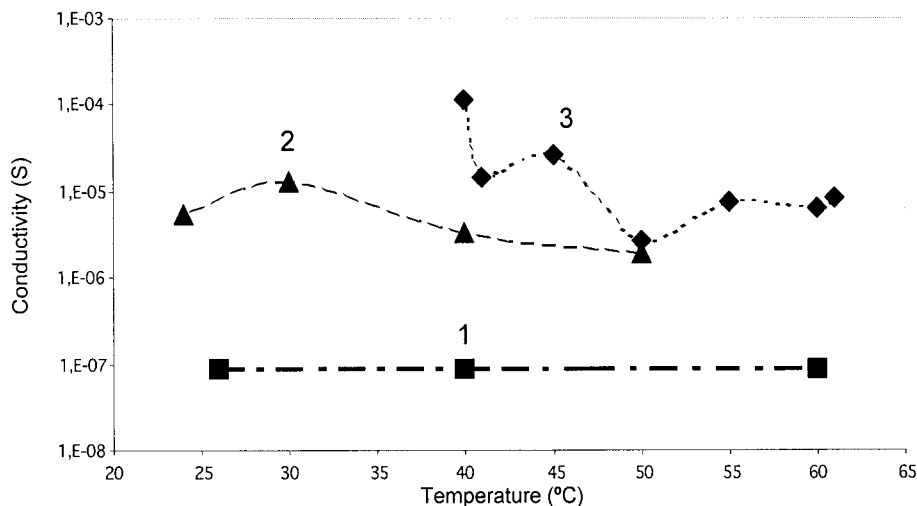
Figure 3 Surface conductivity of ABS samples covered with PANI in the two-step process described in the Experimental section: dependence on the temperature of the aniline solution stabilized with different surfactants: (1) 0.1M sodium dodecyl sulfate, 2% aniline, and 20 min of soaking; (2) 0.1M hexadecyl-trimethyl-ammonium bromide, 5% aniline, and 2 min of soaking; and (3) 0.1M N,N-dimethyl-octalamine-N-oxide, 2% aniline, and 20 min of soaking.

to intensify coating and drastically improve its quality. However, the chemical nature of the surfactant still affected the process.

Thus, in a 0.1M sulfate II solution, increasing temperature to 40°C and then to 60°C resulted in uniform and gradually more greenish PANI films after 20 min of soaking (Fig. 3, curve 1). Nevertheless, the conductivity was measurable only for the sample treated at 60°C (10^{-7} S/□ level). For the bromide III solution, increasing the temperature to 60°C had no effect for a 0.1M concentration (after 20 min of soaking), but an increase in temperature produced a visible coating for the 0.2M bromide III solution. In the last case, the thermal effect was so pronounced that a slight temperature increase (to 30°C) resulted in a visible greenish conductive coating (10^{-5} S/□ level) after just 2 min of soaking (Fig. 3, curve 2).

In the heated 0.1M dimethyl I solution, the ABS samples were treated more intensively than in sulfate II but less than in the bromide III solutions. In this way, the 2-min soaking was ineffective at any temperature, but the 20-min dipping resulted in very profound and intensive coating by PANI. In Figure 3 (curve 3), the conductivity of the coatings obtained after 20 min of soaking for the ABS samples at different temperatures in 2 wt % aniline/0.1M dimethyl I solutions is presented. The conductivity achieved its top level at 40°C and then decreased, keeping a quite high value of 10^{-5} S/□. However, the thermal experiments were poorly reproducible because of aniline volatility at elevated temperatures. The aniline boiling point is 71°C, and prolonged heating of a small amount of the used soaking solution (50 mL) made the aniline concentration easily and disorderly decrease during experiment.

So, in conclusion, the conductive coating of ABS by PANI in a two-step process involving an organic free solvent is feasible, and good quality films with high conductivity can be obtained. For each studied surfactant, we were able to find optimal conditions for controllable and reproducible coating by varying the concentration of aniline and surfactant or the time or temperature of soaking.

SEM micrographs

In Figures 4–8, the SEM photos of the ABS samples coated by PANI in the proposed organic free solvent method are shown. A pair of pictures is presented for each sample: one is a general view at 250×, and the other is a microview at 2500×.

In Figures 4–6, the surface views of untreated ABS and ABS covered by PANI in sulfate II and bromide III solutions are presented. The untreated ABS sample possessed a tightly packed dense surface morphology [Fig. 4(A)], but at higher magnification [Fig. 4(B)], the small lumps of the different polymer components (acrylonitrile, butadiene, or styrene) were noticeable as soon as ABS was a triblock copolymer.

The coating of ABS by PANI from the sulfate II solution was uniform, although macrosize particles of irregular shape (several micrometers) were occasionally seen on the surface [Fig. 5(A)]. Despite this, the body of the ABS sample was continuously covered by microgranules of PANI 300–500 nm in diameter that overlapped and merged on the substrate surface [Fig. 5(B)]. Although the morphology of ABS itself was not seen, it could be deduced quite easily.
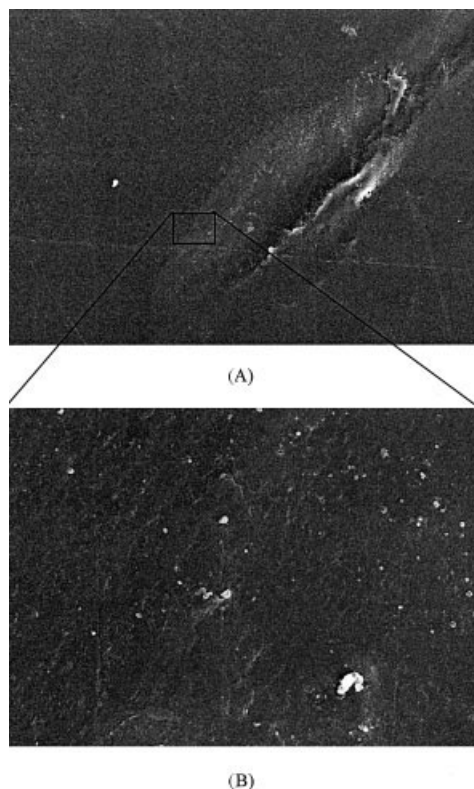
Figure 4 : Scanning electron micrographs of the untreated ABS sample at different magnifications: (A) 250 and (B) 2500×.

PANI coating from the bromide III solution was also very uniform and generally quite similar to the previous case. Nevertheless, the macrosize particles were more spherical and larger [to 15–20 μm, Fig. 6(A)], and the microgranules of PANI were deposited closer to the ABS surface. These last seemed to be more separate one from another and lesser merged [Fig. 6(B)], and their size was about 500–1200 nm.

Very different SEM photos were taken with ABS coated by PANI from the dimethyl I solution. Figures 7 and 8 show photos for 2- and 5-min treatments at ambient temperature. For shorter times, the PANI film was extremely irregular, and large areas of the ABS surface were left uncovered [Fig. 7(A,B)]. Increasing the dipping time led to the etching of ABS surface so that very profound cracks appeared on it [Fig. 8(A)]. At the same time, all of the surface area was coated by PANI globs. The size of these granules did not increase with dipping time in the dymethyl I solution, and it was as big as 1–2 μm [cf. Figs. 7(B) and 8(B)]. We believe that in the dimethyl I solution, the selectivity of aniline absorption by different components of ABS was clearly revealed so that blocks of different chemical composition were decorated by PANI.

DISCUSSION

The proposed method for the deposition of conducting PANI on the surface of ABS was based on permeability of aniline into the ABS matrix. The use of diluted solutions instead of pure aniline permitted us to regulate absorption and reduce the rate of polymerization. In the reported organic free solvent method, the dilution of pure aniline was achieved with an emulsion stabilized in the presence of surfactants. The ultrasonification of the immiscible combination of water and aniline allowed us to prepare stable homogeneous solutions/emulsions and to produce PANI coatings of excellent quality. The chemical nature of surfactant tuned the method in what affected the particular conditions of the aniline/surfactant solution preparation, its optimal concentration, and other parameters of treatment, such as the time and temperature of soaking. We believe that for each possibly used surfactant, the optimal adjustments could be found.

The method based on water emulsions was better than an original one that used ethanol/aniline mixtures: the optimal aniline concentration was less (2–5 wt % vs 10–15 wt % in ethanol), and the time of treatment was shorter (1–10 min vs 15–20 min in eth-
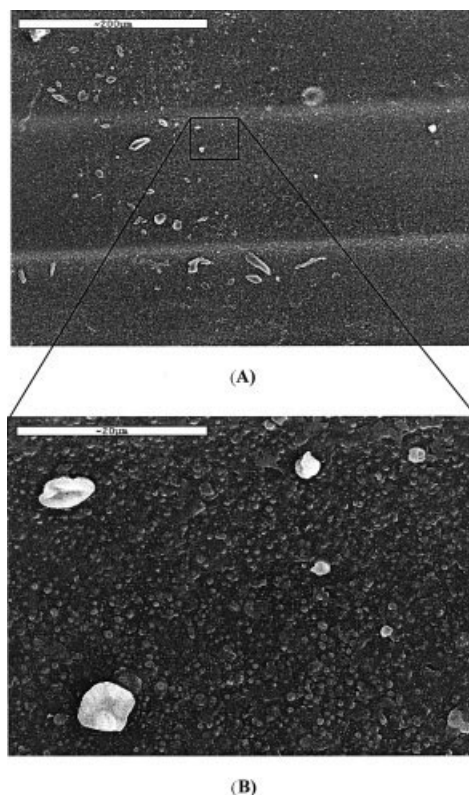

Figure 5 Scanning electron micrographs of the ABS sample treated in a 5% aniline solution with sulfate II surfactant at room temperature (~26°C) for 5 min. Oxidative polymerization of the absorbed aniline was done as described in the Experimental section. Magnification: (A) 250 and (B) 2500×.
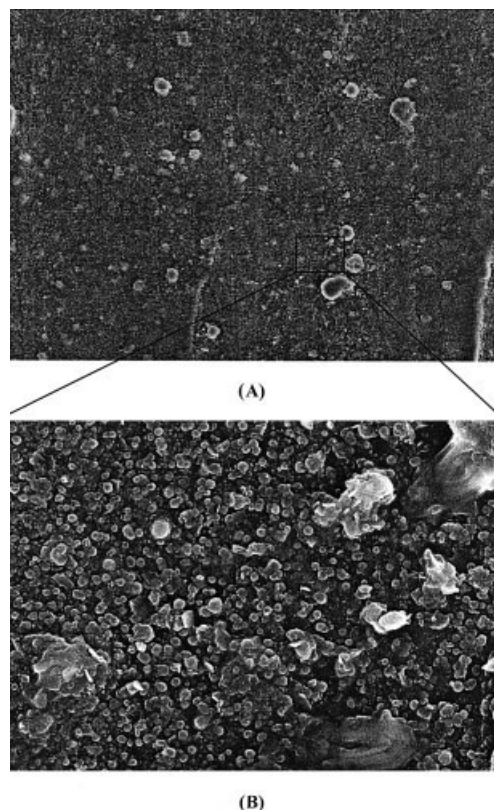
Figure 6 Scanning electron micrographs of the ABS samples treated in a 5% aniline solution with bromide III surfactant at room temperature (~26°C) for 2 min. Oxidative polymerization of the absorbed aniline as described in the Experimental section. Magnification: (A) 250 and (B) 2500×.

anol). Second, a very important aspect, the safety conditions were improved; water is much more eco-friendly and secure than alcohol-based organic media.

Depicted in Scheme 4 is the probable route for the adsorption and absorption of aniline on the ABS surface. At first, after the immersion of the sample into the emulsion, the aniline bubbles simply adhered to the surface [Scheme 4(a)], and their concentration was small. Then, they spread onto the surface [Scheme 4(b)] and covered the polymer with a thin film [Scheme 4(c)]. The absorption (penetration) of aniline into ABS began when the aniline molecules established a contact with the ABS surface. By varying the time and temperature of soaking, we easily achieved control of the absorption. From this point of view, the maximum conductivity after treatment could be related with the moment of maximum coverage of the ABS surface by aniline drops. The adhesion of deposited PANI to ABS reflected the depth of aniline penetration into the polymer matrix. Different sized PANI granules after treatment were related to the mean size of aniline drops in the emulsion.

The SEM photos clearly show that the average size of PANI granules varied from one surfactant to an-

other. As shown in Scheme 4, the size of emulsion drops controlled the mean distance between them at a given concentration and, probably, the thickness of the aniline film on the ABS surface. However, the nature of surfactant should have controlled the ability of the ABS surface to trap the drops. As soon as the ABS was a triblock copolymer, the fine difference in the liophility of its components to different surfactants led to the accumulation of aniline drops in certain zones that were further decorated by PANI. Perhaps we observed such behavior in case of the dimethyl I surfactant (see Figs. 7 and 8). The same decorative behavior could be expected for the coating of materials with porous morphologies.

The selectivity of each ABS component to aniline absorption is another point to discuss. From a general chemical approach, we could expect that some components of a copolymer, because of its chemical nature (their functional groups), would be more able to absorb aniline than others and, consequently, would be more treatable in the proposed method. Determining such functional groups should help in to extend the method to other polymers in addition to ABS. Works are in progress, and preliminary experiments have shown that a polystyrene component could not be
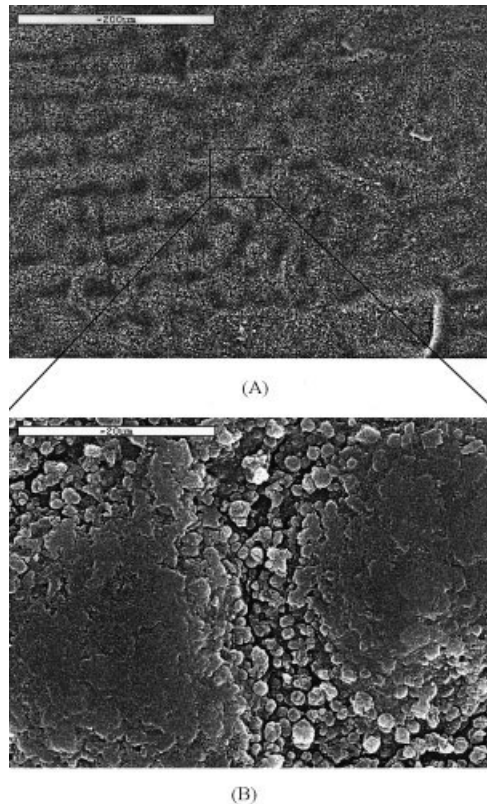

Figure 7 Scanning electron micrographs of the ABS samples treated in a 5% aniline solution with dimethyl I surfactant at room temperature (~26°C) for 2 min. Oxidative polymerization of the absorbed aniline as described in the Experimental section. Magnification: (A) 250 and (B) 2500×.

covered by PANI, but two others (polybutadiene and polyacrylonitrile) should, as well as poly(methyl acrylate) (PMA), another larger commercialized plastic. PMA is often used as a substrate in thin-film electro-optical devices. The adjustment of the presented method for PMA could open new possibilities in the optical quality conductive coating of insulating organic supports.

CONCLUSIONS

An improved method for the conductive coating of ABS polymer by PANI was proposed. In the first soaking step of the method, a fine emulsion of aniline in water stabilized by surfactants was used, and in the second step, an acidic peroxidisulfate ammonium solution oxidatively polymerized the aniline adsorption and was absorbed by the ABS matrix. A conductive PANI film of excellent quality was formed after treatment. The chemical nature of the surfactant affected the particular settings of the aniline/surfactant emulsion preparation and its working conditions (optimal concentration and time and temperature of soaking),
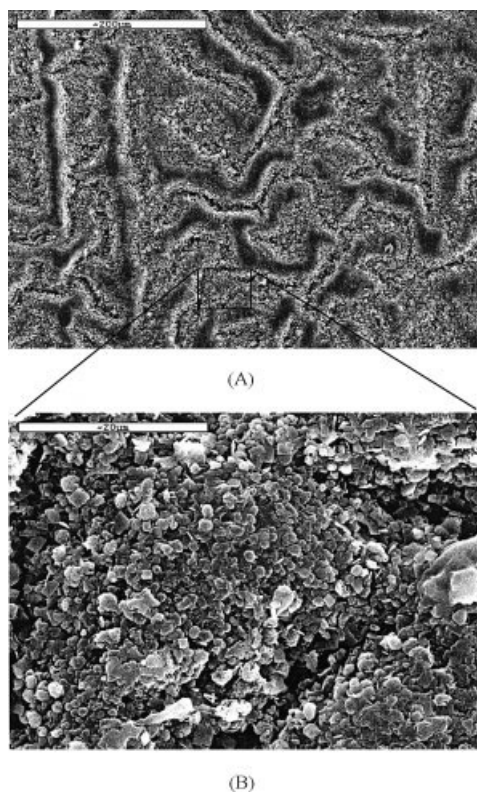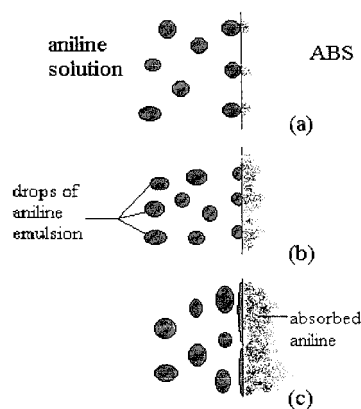
Scheme 4 Probable route for the adsorption and absorption of aniline at the ABS surface.

so that for any possibly used surfactant, the optimal adjustments could be done.

Suggestions on the operation mechanism of the organic free solvent method have been put forward. We proposed that microdrops of aniline were formed during the emulsion preparation and that the size of the drops depended on the surfactant nature and aniline/surfactant molecular ratio. These drops adhered to the ABS surface and spread onto it during the soaking step with the simultaneous penetration of aniline into the polymer. Maximum conductivity after whole treatment was reached if the maximum coverage of the surface by aniline drops was achieved in the soaking step.

The proposed method could be extended over other conventional polymers if the polymers are able to absorb aniline (be swollen). The chemical nature of polymer components (existing functional groups) and the morphology package should be the factors that define the applicability of the proposed method to new classes of polymers.

Figure 8 Scanning electron micrographs of the ABS samples treated in a 5% aniline solution with dimethyl I surfactant at room temperature (~26°C) for 5 min. Oxidative polymerization of the absorbed aniline as described in the Experimental section. Magnification: (A) 250 and (B) 2500×.

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