# Simple Chemical Polymerization Method for Deposition of Conducting Polyaniline on Surface of Acrylonitrile Butadiene Styrene

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**ABSTRACT:** A simple method of depositing a uniform layer of polyaniline (PANI) on the surface of acrylonitrile butadiene styrene (ABS) is described. The method consists of two steps, in which the first step is composed of soaking of ABS in aniline solution, and the second step consists of polymerization of aniline absorbed inside the ABS matrix by an oxidant. The ABS surface is seen to be completely masked by the PANI layer when it is coated from solution containing 10 or 15% of aniline. The surface resistance of the ABS plate, which is coated from a solution containing 15% aniline, shows resistance of 30 k$\Omega$ and rises up to 400 k$\Omega$ as concentration of aniline in the solution is decreased to 5%. From scanning electron micrographs, a granular growth of PANI is noticed on the ABS surface. Thermal gravimetry–mass spectroscopy data reveal that coating the ABS plate with PANI does not weaken an ABS matrix. The adherence of PANI on the ABS surface is explained on the basis of interaction between the aniline and cyano group from the acrylonitrile moiety of ABS. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1904–1910, 2002

**Key words:** polyacrylonitrile butadiene styrene); conducting polymers; surface modification; morphology

## INTRODUCTION

In the past couple of years, significant work has been done on combining electrical properties of conducting polymers such as polyaniline (PANI) with mechanical properties of insulating polymers to produce conducting composites or blends which are useful in certain applications, such as antistatic coating, and electromagnetic interference shielding.[1–4] Such composites can be produced either by thermal processing or by solution-casting method.[5–8]

PANI protonated with inorganic acids such as HCl or $H_2SO_4$, unstable above 150°C, cannot be used for thermal processing with most of the commercial plastics such as acrylonitrile butadiene styrene (ABS) or polyethylene terephthalate (PET). Although efforts were made to increase processibility and stability of PANI by using phosphoric acid diesters as a dopant, the time required to prepare these dopants and the cost involved in it makes this process unsuitable at a commercial level.[9,10] On the other hand, camphor sulfonic acid (CSA)-doped PANI can be used to prepare soluble PANI particularly in *m*-cresol, and hence, it is possible to obtain composites with different insulating matrices by the solution-casting method. However, the solution-casting method does not seem to be ecofriendly, as evaporating

phenolic solvents such as *m*-cresol is hazardous, and moreover, it takes several days to evaporate it completely.

It is therefore important to develop a simple method which can render these plastics conducting. Earlier, some efforts were made in this regard, especially to coat polymers such as poly(vinyl chloride and polymethyl methacrylate by diffusion oxidation process and dip-coating methods, respectively.[11,12] However, no such method was formulated for ABS in spite of having tremendous application potential.

In the present work, we have utilized an interaction between aniline and ABS to incorporate aniline molecules into the surface layers of ABS and then polymerize them directly within the polymer matrix. The ABS samples coated with polyaniline were characterized by different techniques and the results are reported here.

## EXPERIMENTAL

Aniline solutions of different concentrations were prepared in ethanol. Both chemicals were purchased from Sigma–Aldrich and aniline was distilled prior to use. The ABS plates obtained from industry were washed with ethanol and dried in a vacuum oven for 24 h. The as-treated ABS plates, measuring $10 \times 1$ cm, were dipped in aniline solution for different time intervals and then washed with water to remove the excess aniline from the surface. The plates were transferred into the $0.5M$ $(NH_4)_2S_2O_8$ solution prepared in $1.5M$ HCl for a period of 10 min. Finally, ABS plates coated with PANI were removed, washed, and kept under dynamic vacuum for 48 h. The as-deposited plates were utilized for further measurements.

The surface resistance of ABS plates (Ube Cycon Company, Japan) coated with conducting film was measured by the two-probe method. The finely polished Cu wires were contacted on the ABS plate by using silver paste and the contact was sealed with the help of epoxy resin. The surface resistance was measured with a Hokuto-Denko galvanostat (model HA-501). Scanning electron micrographs were taken on a JEOL JSM 6300 scanning electron microscope (SEM). The samples were coated with gold ($\sim$ 20 nm) before SEM measurements. Thermal gravimetry–mass spectroscopy (TG-MS) analysis was performed on a JEOL MS-TG/DTA (model 220) under He atmosphere. The temperature was changed from 40 to 900°C at the programmed heating rate of 5°C/min.

## RESULTS AND DISCUSSION

In a two-step method for coating ABS with PANI as described above, it is necessary to optimize various parameters to obtain uniform and adherent deposition of PANI. The concentration of aniline in the dipping solution, the solvent, and the dipping time are the three parameters that could be varied in the first step. It is reasonable to assume that after immersing the ABS plate in aniline solution some aniline molecules get entangled with ABS matrix, whereas few get adsorbed on the ABS surface. The above speculation is based on the fact that ABS is not resistant toward aniline and the permeation of aniline molecules into ABS is quite feasible. This was also reflected in increased uptake of aniline by ABS on increasing the concentration of aniline in the solution as well as the dipping time of ABS in this solution. It is interesting to note that in pure aniline as a solvent, the interaction of aniline with ABS is so profound that the sample becomes sticky in a few minutes. Therefore, the role of solvent in our method is to control the absorption of aniline on ABS by decreasing its concentration. Thus, the entangled aniline provides the basis of adherence for PANI and those molecules adsorbed on the ABS surface initialize the polymerization after transferring the sample into the $(NH_4)_2S_2O_8$ oxidant solution during the second step of processing.

One can change the variety of parameters in the second step of PANI coating such as concentration of oxidant, its chemical nature, amount of protonic acid, and the processing temperature. However, we have not made alterations in any of these parameters and conditions were kept constant as described in the experimental part. The main process which occurs during the second step is the slow development of oxidative polymerization of absorbed aniline through the ABS matrix. Some induction period, similar to that observed in the chemical polymerization of aniline in solution, is noticed and the uniform greenish coloration of polyaniline emeraldine salt on the ABS surface appears gradually after 2–5 min. The color becomes more intense with respect to time and approximately after a 10-min interval it does not change anymore, signifying the total consumption of aniline absorbed by ABS matrix. It is worth
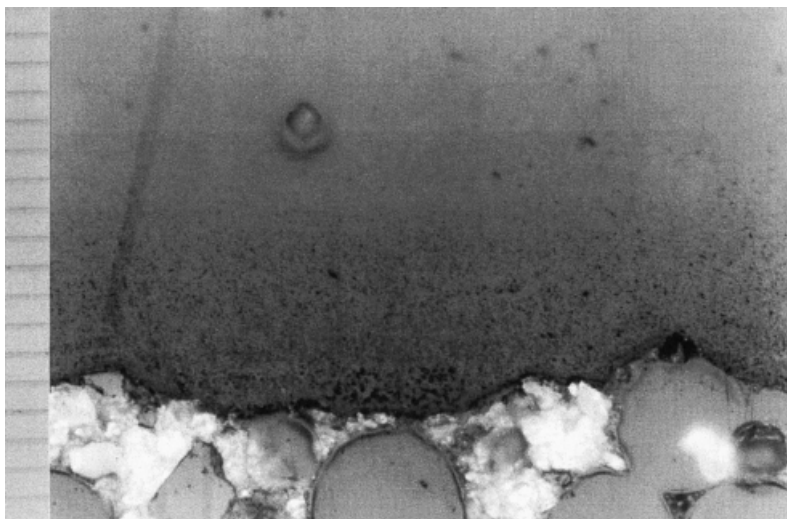
**Figure 1**   Cross-sectional view of ABS plate coated with polyaniline at a magnification of 400×. Left bar is a micrometric scale at the same magnification. Concentration of aniline in dipping solution was kept to 15%; dipping time was 5 min.

mentioning here that PANI coating affects the very thin surface of ABS layer (a few microns), whereas the bulk of the ABS layer is seen to remain unaffected as observed visually by breaking the PANI-coated ABS sample and also from the cross-sectional view of the ABS sample coated from 15% aniline solution (Fig. 1).

Table I gives the surface-resistance values of PANI-coated ABS plates obtained at different aniline concentrations. The pure ABS plate shows the resistance of $10^{14}$ $\Omega$, indicating its insulating behavior. However, after coating ABS with PANI, the resistance is found to decrease significantly. The ABS plate coated from solution containing 15% of aniline possesses surface resistance of 30 k$\Omega$. Perhaps this value is close to the minimum

**Table I   Surface Resistance of ABS Plates Coated with PANI**

| Sample No. | Concentration of Aniline (%) | Resistance ($\Omega$) | Soaking Time in Aniline (min) |
|---|---|---|---|
| 1 | 5 | $4 \times 10^5$ | 20 |
| 2 | 10 | $2 \times 10^5$ | 10 |
| 3 | 15 | $3 \times 10^4$ | 5 |
| Blank | 15 | $>10^{14}$ | 5 |

Blank: ABS plate soaked in 15% aniline. Samples 1, 2, and 3 were dipped in $(NH_4)S_2O_8$ for 10 min. Resistance values are extracted as a mean value after measuring resistances of five samples prepared under similar conditions. The deviation in resistance value was found to be around 2 k$\Omega$.

surface resistance that could be achieved by our method. By decreasing the aniline concentration in solution from 15 to 5%, the resistance shoots up to a value of 400 k$\Omega$. The intermediate concentration of aniline in solution (i.e., 10%), however, reveals resistance around 200 k$\Omega$.

It is important to mention here that the soaking time of the ABS plate in aniline solution was optimized on the basis of quality and resistance of deposition. Thus, for 5% aniline concentration in solution and soaking time of 5 min, the deposition of PANI on the ABS plate was not uniform; instead, PANI was visible on the ABS plate in the form of several patches. The uniform deposition was observed at only 20-min dipping time. On the other hand, for 10% aniline concentration in solution, at a lower dipping interval of 2 and 5 min, a thin film of PANI was visible on the ABS surface. However, the surface resistance of PANI coating was found to be higher than that of the ABS plate soaked for 10 min (i.e., 5 M$\Omega$ and 500 k$\Omega$ for 2 and 5 min dipping time intervals, respectively). In the case of 15% aniline quantity in solution, the coating was found to be more uniform at a 5-min dipping time interval than lower time intervals.

It will be interesting to perform the in-depth resistance as well as the time-dependent stability measurements on such ABS-coated polymer samples; currently the work is in progress in our laboratory. However, our preliminary data on the time-dependent stability reveal that the resis-
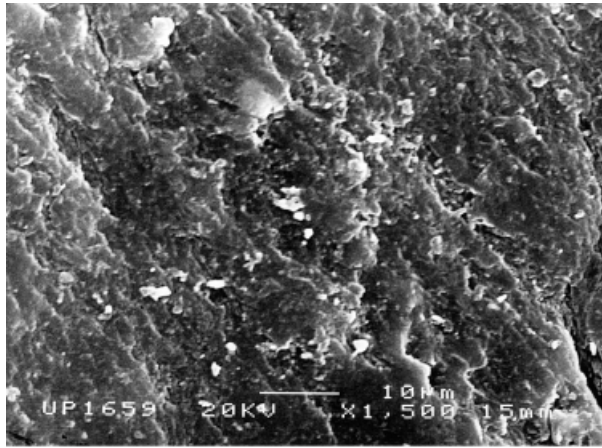
(a)
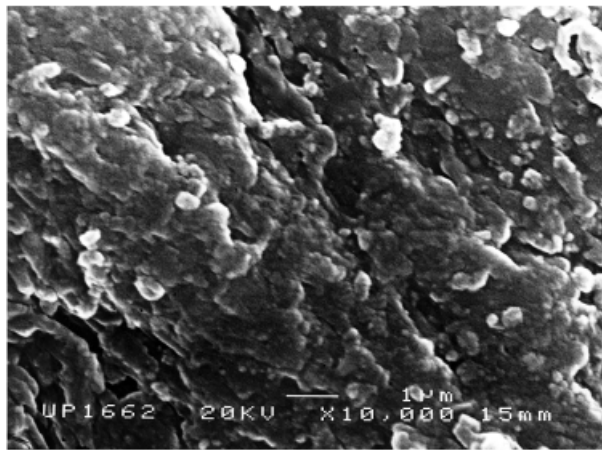


(b)

**Figure 2** Scanning electron micrographs of pure ABS taken at magnifications of (a) 1500× and (b) 10,000×.

very smooth either. After dipping the ABS plate into ethanol solution containing 15% aniline monomer, the surface of ABS becomes more uniform due to the absorption of aniline and it is reflected at low magnification of 1500× [Fig. 3(a)]. The morphological features become much clearer at a higher magnification of 10,000× [Fig. 3(b)] and one can notice a modified ABS surface which is much smoother than pure ABS. The little swelling of the ABS matrix observed in the micrographs do indicate that aniline interacts with the ABS matrix.

The micrographs of ABS coated with conducting PANI after dipping ABS plates in 5, 10, and 15% solution of aniline are depicted in Figures 4-6, respectively. On comparing Figures 4–6, one
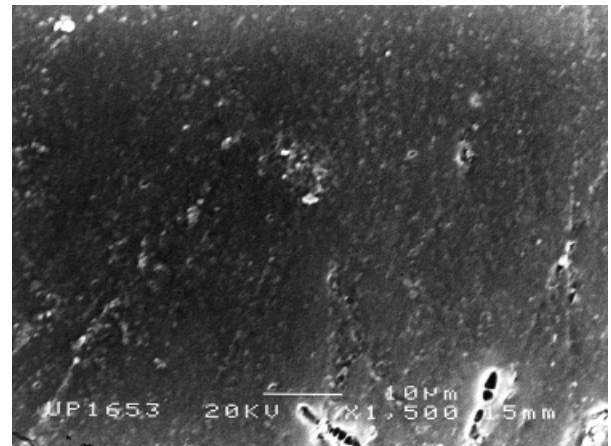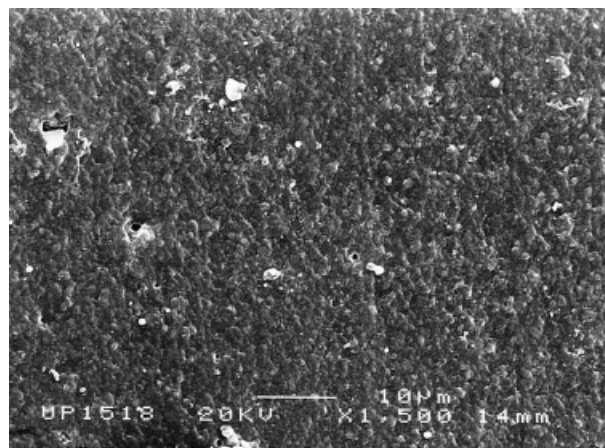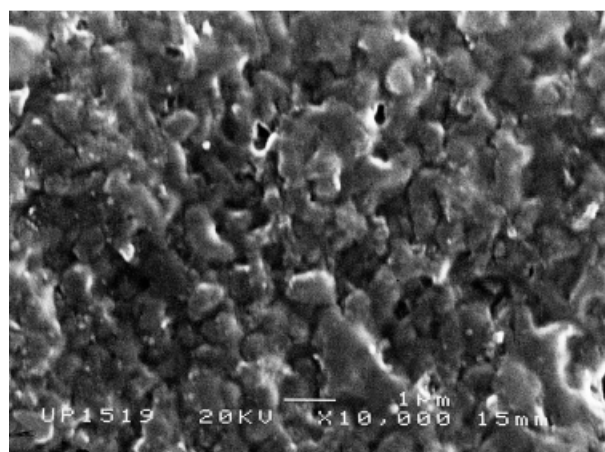


(a)
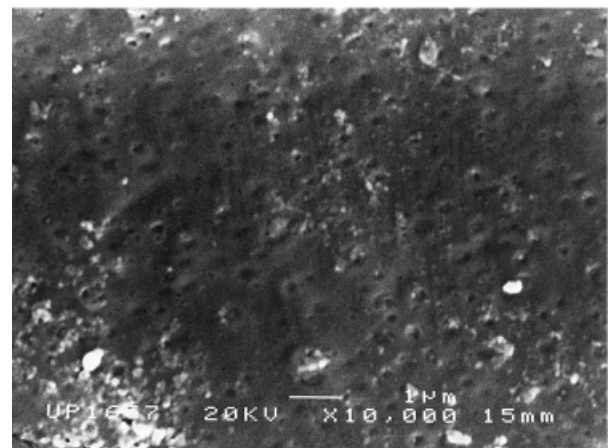


(b)

**Figure 3** Scanning electron micrographs of ABS plate after dipping it in 15% aniline–ethanol solution for 5 min at magnifications of (a) 1500× and (b) 10,000×.

tance of the ABS sample coated from 15% aniline solution increases by two orders of magnitude (approximately 5 mΩ) after a period of 10 months. Other samples behave similarly. Thus, the proposed method allows us the flexibility in preparing the PANI-coated ABS plates of different resistance by changing the monomer concentration together with the soaking time of the ABS matrix in the solution.

Figures 2 and 3 represent scanning electron micrographs of pure ABS and the ABS plate dipped in 15% aniline solution, respectively. ABS being a triblock copolymer reveals a spongy type of morphology [Fig. 2(a,b)]. At a higher magnification of 10,000×, lumps of different sizes arising from acrylonitrile or butadiene or styrene are clearly evident in the micrographs. At lower magnification, the surface of ABS is not seen to be
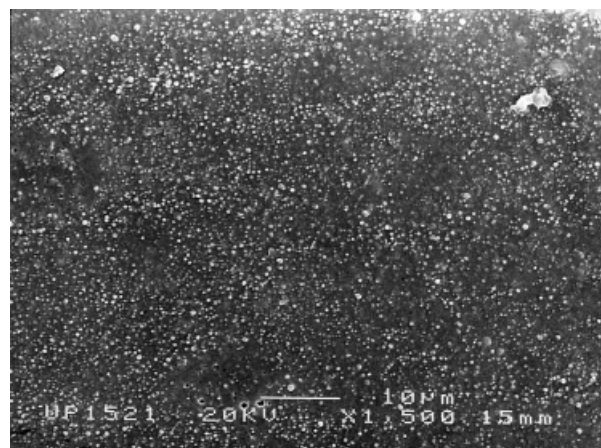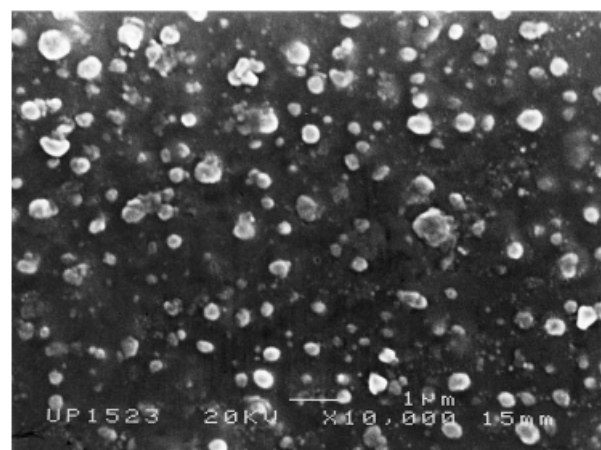
(a)



(b)

**Figure 4** Scanning electron micrographs of ABS plate coated with polyaniline at magnifications of (a) 1500× and (b) 10,000×. Concentration of aniline in dipping solution was kept to 5%; dipping time was 20 min.

can observe a gradual variation in the morphological features as a function of aniline content in dipping solution. At a lower concentration of aniline monomer in solution, the surface of ABS is still evident and is especially seen at 10,000× (Fig. 4). However, the lumps of each block of acrylonitrile or butadiene or styrene are seen to be completely covered with PANI. One can see very close contact of PANI particles grown on core shells of ABS and this might be the reason the ABS plate coated with PANI at this concentration of aniline monomer shows a significantly lower value of resistance than that of pure ABS. The micrograph at lower magnification, however, reveals a smoother surface than pure ABS [Fig. 4(a)].

As the concentration of aniline rises to 10%, the surface of ABS does not appear in the micrographs even at higher magnification [Fig. 5(b)]. Instead, a uniform layer of PANI deposited on ABS plate is clearly observed [Fig. 5(a,b)]. The coated layer thus completely masks the original morphological features of ABS. The average size of PANI granules ranges between 250 and 500 nm. By further increasing the concentration of aniline to 15%, a dense population of PANI particles is noticed on the ABS surface [Fig. 6(a,b)]. The size of PANI particles is also seen to be increased. The average particle size lies between 250 and 600 nm. The morphology appears to be similar to fine pebbles collected in small vessel
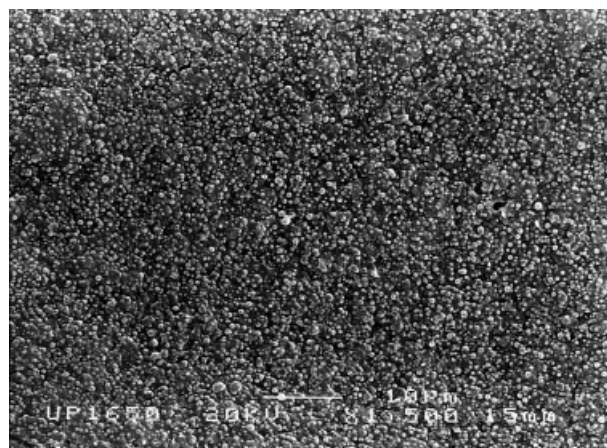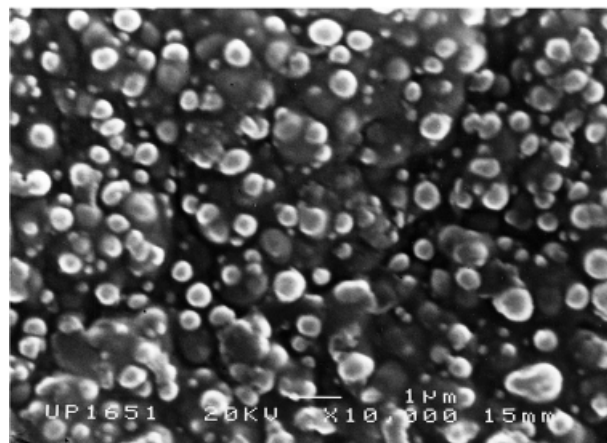


(a)



(b)

**Figure 5** Scanning electron micrographs of ABS plate coated with polyaniline at magnifications of (a) 1500× and (b) 10,000×. Concentration of aniline in dipping solution was kept to 10%; dipping time was 10 min.

which adjust themselves in such a way that they give rise to a very small dimension void (lesser in dimension than the original pebbles) [Fig. 6(b)].

Further, to check whether PANI coating on ABS plate affects the thermal properties of ABS, we have recorded TG-MS analysis of pure ABS and ABS coated with PANI from 15% aniline concentration in solution. The decomposition of the ABS matrix starts slowly at 220°C and a brisk breakdown is noticed above 360°C, which continues up to 460°C. As the quantity of PANI coating on ABS is very small, mass fragments related to PANI are not observed clearly in the mass spectra recorded simultaneously with thermal patterns. A single-stage thermal pattern, however, reveals
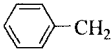
**Table II  Mass Fragments of ABS at 360°C**

| Mass No. | Fragments Obtained |
|---|---|
| 41 | $CH_2–CH–CH_2$ |
| 51, 78 | ⬡ |
| 67 | $CH_2–CH_2–CH=CH–CH_2$ |
| 91 | ⬡–$CH_2$ |
| 104 | $CH_2-CH$ / ⬡ |
| 117 | $CH_2-CH_2-CH$ / ⬡ |
| 133 | $CH_2-CH_2-CH_2-CH$ / ⬡ |
| 144 | $CH=CH-CH_2-CH_2-CH$ / ⬡ |
| 170 | $CH-CH_2-CH=CH-CH_2-CH_2-CH$ / ⬡ |



(a)



(b)

**Figure 6** Scanning electron micrographs of ABS plate coated with polyaniline at magnifications of (a) 1500× and (b) 10,000×. Concentration of aniline in dipping solution was kept to 15%; dipping time was 5 min.

various fragments due to ABS at 360°C (Table II). Both materials reveal similar thermal patterns with total weight loss of 98.47 and 98.66% for pure ABS and ABS plate coated with PANI, respectively, at the end of the experiment (900°C). Because the nature of thermal profiles obtained for pure ABS and ABS coated with PANI is similar, one can clearly state that the PANI-coated ABS matrix is not weaker than the original polymer matrix.

The interaction of aniline with ABS might be explained on the basis of Scheme 1. The amine group of aniline possibly interacts with either of the three groups from ABS (i.e., either CH=CH group from butadiene, phenyl group from styrene, or C≡N group from acrylonitrile). However, among these three, the C≡N group is seen to be most reactive. It could react with the amine group of aniline as mentioned in Scheme 1 and then act as a nucleation center where the further polymerization process is initialized once the ABS has been transferred to oxidant solution.

## CONCLUSION

The surface of the ABS polymer can be made conductive by a simple chemical polymerization
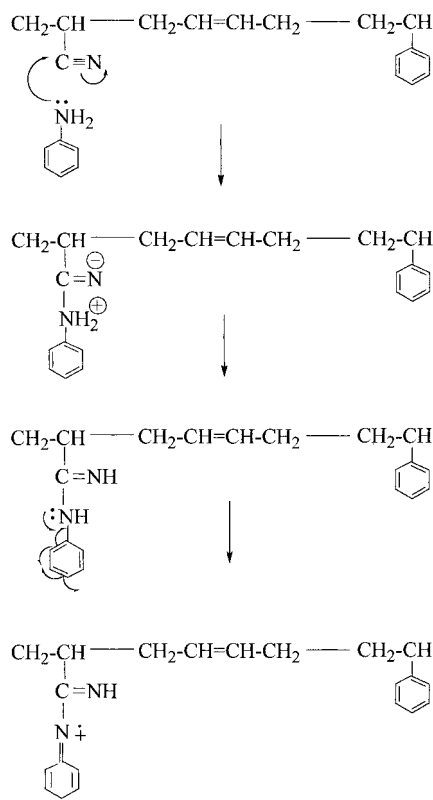
**Scheme 1**  Interaction of aniline with ABS matrix.

method consisting of two steps: (1) soaking of ABS in aniline solution and (2) polymerizing the aniline absorbed inside the ABS matrix by an oxidant. After coating with PANI, the surface resistance of ABS is found to decrease significantly (i.e., more than nine orders of magnitude). The conducting coating of PANI shows good adherence to ABS substrate and this technique seems to be promising for preparing a conducting ABS in EMI shielding and antistatic applications. Although coating of PANI on ABS does not seem to affect the electrical and thermal properties of underlying ABS matrix, more work needs to be done to check the in-depth resistance and mechanical properties of coated material.

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