

Preparation and Characterization of Conducting Polymer Coating on ABS Substrate

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ABSTRACT: Conducting polymer coatings on ABS were prepared by dipping them into *m*-cresol solutions containing polyaniline (PANI), poly(*o*-toluidine) (POT), and poly(*o*-anisidine) (PoAN) protonated with dioctyl hydrogen phosphate (DiOHP) in the presence and absence of polystyrene (PS). The surface resistivity of ABS plates coated with DiOHP-doped PANI in the presence and absence of PS were 5.3×10^7 and $3.0 \times 10^5 \Omega$, respectively. The ABS plates coated with DiOHP-doped PoAN and -doped POT showed higher resistivities (4.2×10^9 and $2.4 \times 10^7 \Omega$, respectively) than that with DiOHP-doped PANI. Although the conductivity of the coated ABS with DiOHP-doped PANI was less in the presence of PS, the permanency and uniformity of the coating, which are very important for practical use, were much improved. Coatings and the coated ABS were characterized by X-ray diffraction, TG/MS, SEM, and reduced viscosity measurements. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2661–2669, 2001

Key words: DiOHP-doped POT; DiOHP-doped PANI; ABS; composite; polystyrene

INTRODUCTION

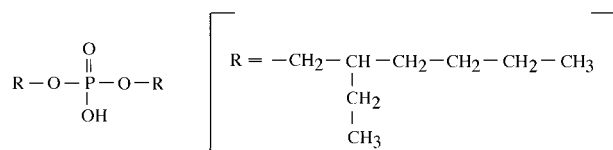
During the past few years, significant progress has been made in the processing of conducting polymers, especially polyaniline and its substituted derivatives.^{1–4} The problem of insolubility of these polymers in common organic solvents was solved by doping them with large functionalized protonic acids, whereas their poor mechanical properties were improved by combining them with some insulating matrixes.^{5,6} Such composites are generally prepared by the solution-casting technique and find application in ESD/anti-static technology or in corrosion protection. However, deterioration of properties cannot be ruled out during the preparation, because one has to dissolve conducting and insulating polymers in the same solvents, often at high temperatures.

Another approach has been done by a few authors in which a guest monomer (e.g., aniline) impregnated in the host polymer is polymerized.^{7,8} In such a process, the host polymer is not changed qualitatively, and the improvement of the electrical and mechanical properties is limited by the content of host and guest polymers. An increase of the ratio of the guest polymer in the composite leads to an enhancement of conductivity but also to a decline of mechanical strength.

In the present work, we therefore developed a simple dip-coating method to obtain a thin conductive coating on ABS. The coating adheres well on the ABS surface with good uniformity and is not easily removed by scratching. As the coating is conducting in nature, it can be useful for suppression of an undesirable static charge on the surface of ABS. For this purpose, polyaniline (PANI) and poly(*o*-toluidine) (POT) protonated with dioctyl hydrogen phosphate (DiOHP) and their composites with polystyrene (PS) were used as a coating material, and these composites were

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Scheme 1

characterized by X-ray diffraction, thermogravimetric/mass (TG/MS), SEM, and reduced viscosity measurements.

EXPERIMENTAL

POT was synthesized using a previously reported procedure.⁹ Finely powdered emeraldine base (EB), 0.328 g, was first added to 50 mL of *m*-cresol, and the solution was stirred for 2 h. The concentration of EB (tetramer) in the dark blue-colored stock solution was 15.7 mM. Before use, this solution was sonicated for more than 2 h and filtered with a cotton plug to remove traces of insoluble matter. A stock solution of EB (PANI) plus DiOHP was similarly prepared by dissolving appropriate quantities of each compound in *m*-cresol.

A thin conductive coating on ABS was achieved by dipping an ABS plate into solutions of POT plus DiOHP with and without PS. A plate (7 × 1 cm) of ABS was dipped in each solution for 40 s and then moved into a fume hood to be left for 60 min. The plate was then kept in an oven at 50°C for another 60 min to remove traces of *m*-cresol. Finally, these plates were dried overnight in a vacuum. The coating thus obtained was uniform and did not peel off. The plate was then used for further characterization. The surface resistivity of ABS coated with the conductive film was measured with a Hokuto-Denko galvanostat (Model HA-501) by the two-probe method. The finely polished Cu wires were contacted on the ABS plate using silver paste, and the contact was sealed using epoxy resin. The conductivities of DiOHP-doped POT and its composites with ABS were measured using a comb-shaped Pt microelectrode in the same way as that described previously.⁴

A UV-vis absorption spectrum of an *m*-cresol solution of DiOHP-doped POT was recorded on a Shimadzu double-beam spectrophotometer (Model 2200). The viscosity data of the *m*-cresol solutions containing DiOHP-doped POT and PANI were obtained with an Ostwald-type viscometer

(Sibata No. 3) at 22 ± 1°C. X-ray data of ABS and ABS coated with the DiOHP-doped POT/PS composite, etc. were recorded using CuKα radiation (λ = 1.542 Å; Shimadzu, Model XD-D1). Thermogravimetric/mass (TG/MS) analyses were performed on a JEOL MS-TG/DTA (Model 220) under a He atmosphere at a programmed heating rate of 5°C min⁻¹. The preparation of the sample for TG/MS followed the procedure described elsewhere.⁴ Scanning electron micrographs were taken with a JEOL scanning electron microscope (JSM-840). The samples for this measurement were prepared by sputtering with gold (thickness ~20 nm).

RESULTS AND DISCUSSION

The DiOHP-doped POT was found to be soluble in several common solvents such as *m*-cresol, toluene, and chloroform. The acid center and two hydrophobic groups in DiOHP (Scheme 1) helped solubilize and plasticize the POT as well as to protonate it.

The conductivity of DiOHP-doped POT was about 4 S cm⁻¹. The composite of DiOHP-doped POT with ABS was prepared by the solution-casting method from *m*-cresol, and the percolation threshold was about 4 wt % (Fig. 1). Such a low percolation threshold is attributed to an interpenetrating network morphology.¹⁰ As a method to prepare an antistatic/conducting material for commercial purposes, however, this process may be not feasible since the evaporation of

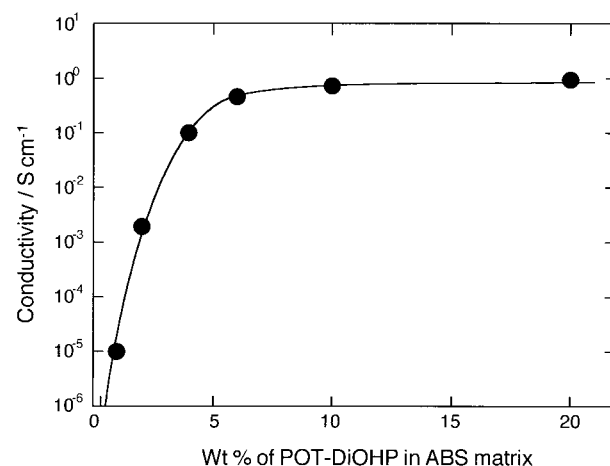


Figure 1 Plot of electrical conductivity of DiOHP-doped POT/ABS composites as a function of the weight percentage of DiOHP-doped POT.

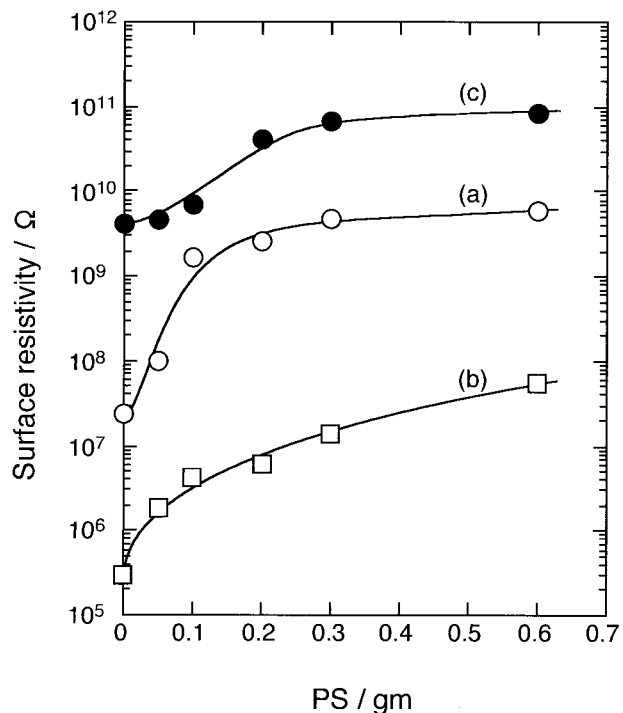


Figure 2 Surface resistivities of ABS plates coated with (a) DiOHP-doped POT/PS, (b) DiOHP-doped PANI/PS, and (c) DiOHP-doped PoAN/PS as a function of the amount of PS. The molar ratio of DiOHP to POT, PANI, or PoAN was always 1.5.

large amounts of *m*-cresol requires many hours. Hence, we attempted to coat conducting POT and its composite with PS on ABS by a one-step dip-coating method. The PS was chosen as an insulating matrix due to its compatibility with ABS. The addition of PS to POT increased the density of the solution and improved the permanency and uniformity of the coating on the ABS substrate.

The surface resistance of the pure ABS plate was 10^{14} to 10^{15} Ω . On the addition of the copolymer (i.e., epichlorohydrin/ethylene oxide), which has been widely used as a commercial antistatic agent, the surface resistance decreased to 10^{10} to 10^{11} Ω . The surface resistivity of the ABS plate was found to be more effectively decreased by coating with various DiOHP-doped polymers (Fig. 2). The ABS plates coated with DiOHP-doped POT/PS composites (curve a) showed the resistivity in the range of 2.4×10^7 to 5.8×10^9 Ω , while those coated with DiOHP-doped PANI and its composites with PS (curve b) decreased to 3.0×10^5 to 5.3×10^7 Ω . A comparison between curves a and b indicates that higher resistivity is observed for the coating of DiOHP-doped POT,

probably caused by the existence of a bulky CH_3 group. The influence of an incorporated bulky substituent on the electrical conductivity was also observed for polyaniline.¹¹⁻¹³ On the other hand, the surface resistivities of the ABS plates with DiOHP-doped PoAN (curve c) were considerably higher than those with DiOHP-doped PANI. This is again owing to the existence of a bulky substituent (OCH_3 group). Low resistivities of both coatings with PANI and POT doped with DiOHP may be useful for the effective suppression of

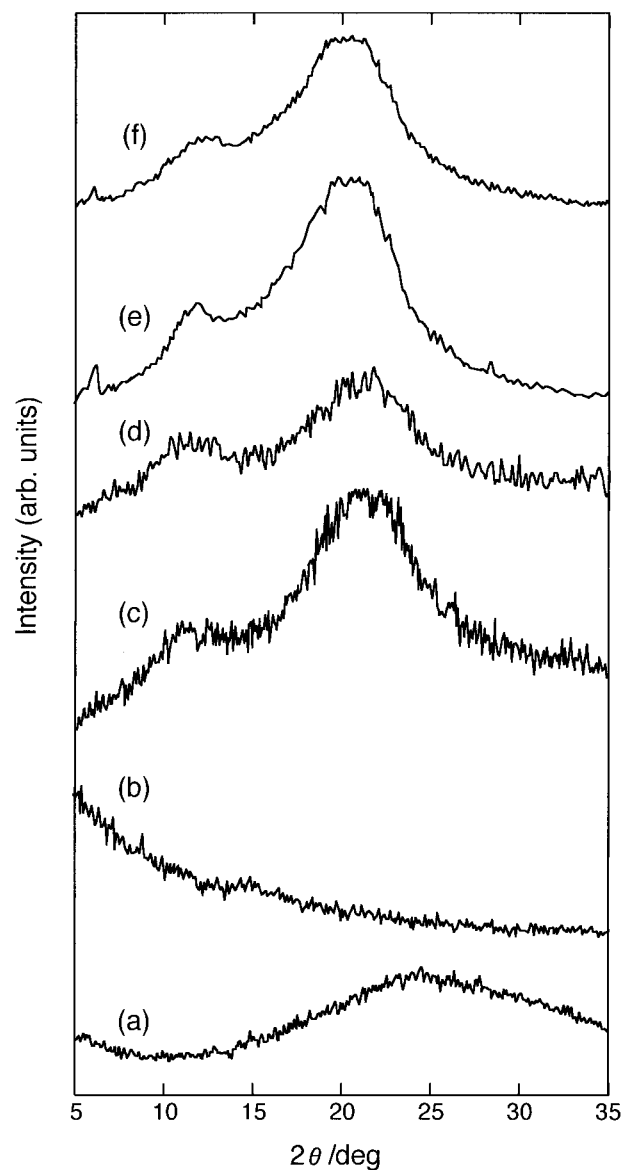


Figure 3 X-ray diffraction patterns of (a) EB, (b) ABS, (c) DiOHP-doped POT, (d) ABS coated with DiOHP-doped POT/PS, (e) DiOHP-doped PANI, and (f) ABS coated with DiOHP-doped PANI/PS.

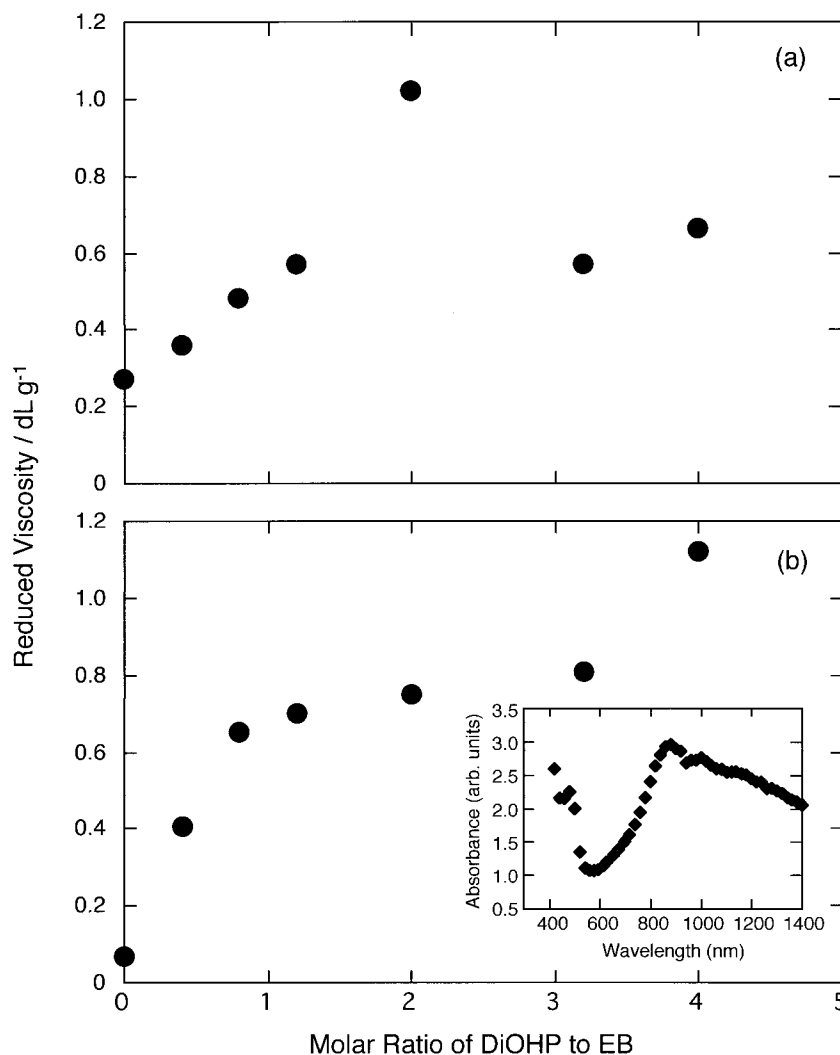


Figure 4 Reduced viscosity of solutions of (a) PANI and (b) POT in *m*-cresol upon the addition of DiOHP. Inset of (b) represents the absorption spectrum of an *m*-cresol solution of DiOHP-doped POT (molar ratio of DiOHP to EB: 2).

undesirable static charging. Moreover, the adhesion of dust on the ABS plates with these coatings was scarcely observed. These coated layers were, therefore, characterized in more detail using various techniques.

X-ray diffraction patterns of (a) EB, (b) ABS, (c) DiOHP-doped POT, (d) ABS coated with DiOHP-doped POT/PS, (e) DiOHP-doped PANI, and (f) ABS coated with DiOHP-doped PANI/PS are shown in Figure 3(a–f). The EB shows a single broad diffuse peak at 24.5° (2θ), suggesting a partly crystalline nature [Fig. 3(a)].¹⁴ Pure ABS is assumed to be amorphous since it does not reveal any peak in the diffraction pattern [Fig. 3(b)]. On the other hand, DiOHP-doped POT shows two

peaks at 21.2° and 12° [Fig. 3(c)]. Such a diffraction pattern of DiOHP-doped POT is not subjected to the influence of the PS matrix and ABS substrate [Fig. 3(d)], indicating that the crystallinity of DiOHP-doped POT is independent of the matrix and substrate. Similar diffraction patterns were obtained for DiOHP-doped PANI [Fig. 3(e)] and ABS coated with DiOHP-doped PANI/PS [Fig. 3(f)]. This is attributed to the similarity in the crystalline properties of POT and PANI.¹² From these results, it is clear that DiOHP-doped POT and -doped PANI are just embedded in the PS matrix without any accompanying chemical interaction. This is in agreement with X-ray photoelectron spectroscopic results in which the elec-

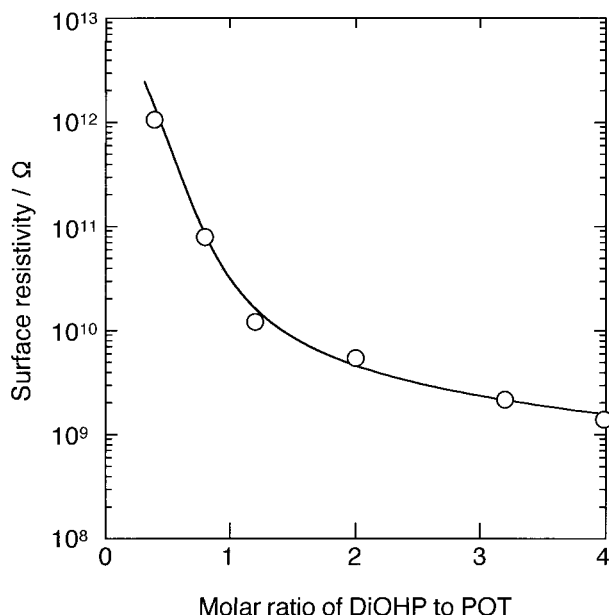


Figure 5 Surface resistivity of ABS plates coated with DiOHP-doped POT/PS as a function of the molar ratio of DiOHP to POT. The amounts of POT and PS were 0.209 and 0.6 g, respectively.

tronic structure of DiOHP-doped PANI blended with PS is not considerably affected by PS and the blend possesses good mechanical properties.¹⁵

The enhanced crystallinity of POT and PANI on doping with DiOHP is related to the change in conformation of POT and PANI in which the coil-like chain opens up and partially straightens out, which, in turn, increases the intermolecular component of the conductivity.¹⁶ The reduced viscosity measurement was performed to obtain information on the change in molecular conformation. The results are shown as a function of molar ratio of DiOHP to EB in Figure 4(a,b). As seen from Figure 4(a), the reduced viscosity of the PANI solution increases with an increase of DiOHP content up to a maximum molar ratio of 2.^{14,17} The initial increase in the viscosity is attributed to the increase in the density of positive charges on the chain. Positively charged chains may repulse each other, resulting in the expansion of the polymer chain. After the polymer chain is fully protonated at the maximum ratio of DiOHP to EB, the conformation tends to become compact coil-like, owing to the screening effect of the H⁺ and phosphate ions formed by the partial dissociation of the excess acid. On the other hand, the maximum molar ratio of DiOHP to EB was observed at 4 for the POT solution, suggesting that a larger amount of acid is needed for the complete proto-

nation of POT [Fig. 4(b)]. Interestingly, POT chains are considered to adopt still expanded coil-like conformation at the molar ratio of 2, because the optical absorption spectrum obtained at the

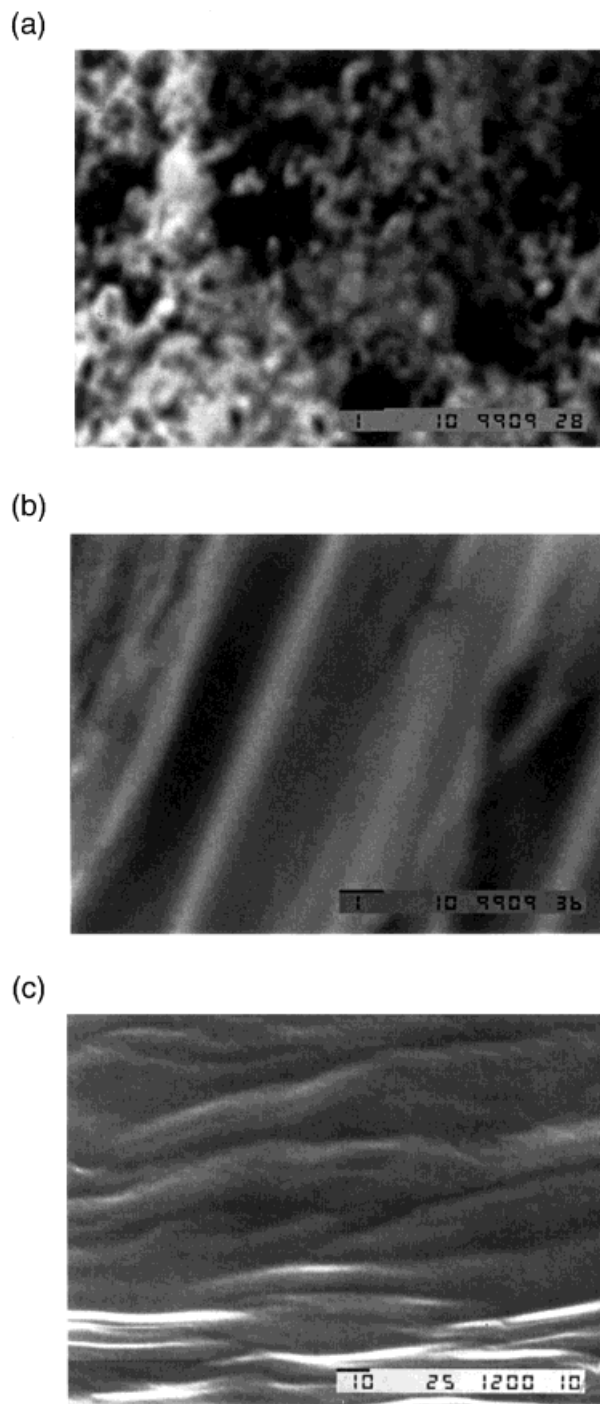


Figure 6 Scanning electron micrographs of (a) pure ABS plate ($\times 10,000$), (b) ABS coated with DiOHP-doped POT ($\times 10,000$), and (c) ABS coated with DiOHP-doped PANI ($\times 10,000$).

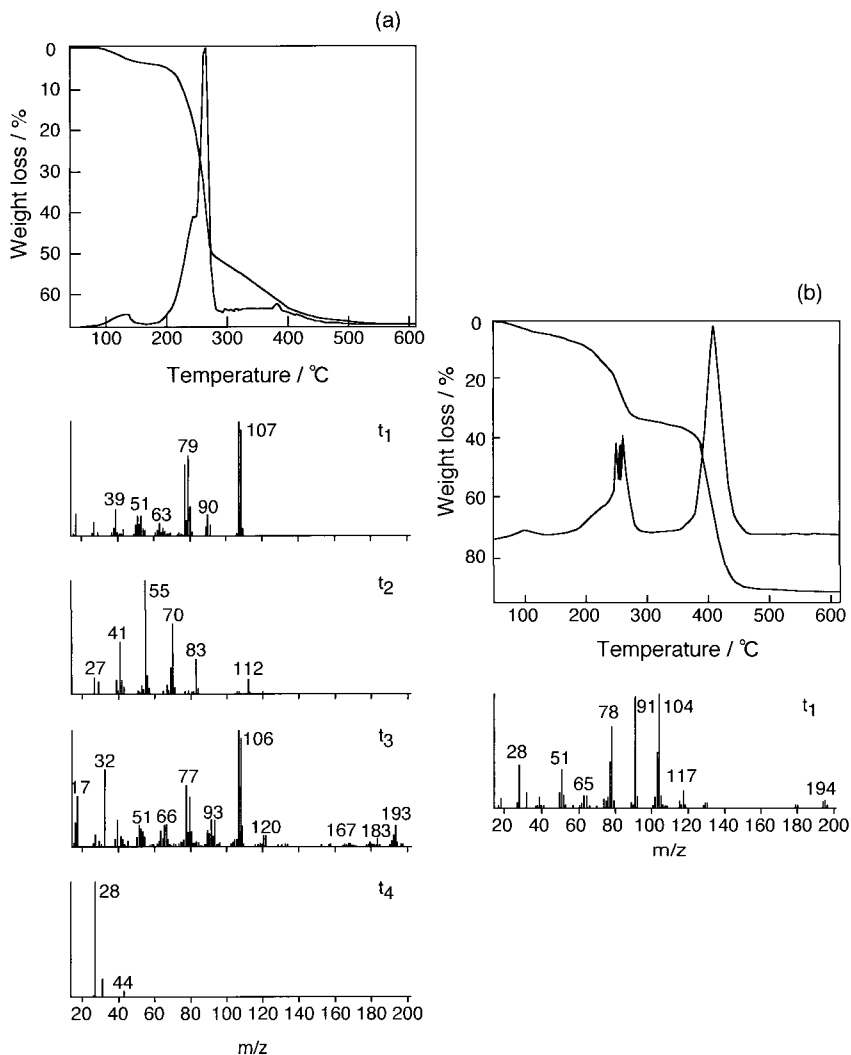


Figure 7 Thermal patterns of (a) DiOHP-doped POT and (b) DiOHP-doped POT/PS taken at a programmed heating scan rate of $5^{\circ}\text{C min}^{-1}$. Mass spectra were simultaneously recorded at different temperatures: (a) t_1 130, t_2 250, t_3 370, and t_4 600°C and (b) t_1 460°C.

same molar ratio [inset, Fig. 4(b)] reveals a free carrier tail at ~ 1000 nm, which is indicative of expanded coil-like conformation.¹⁴ This view is consistent with the results from the measurement of surface resistivity (Fig. 5). The surface resistivities of ABS plates coated with DiOHP-doped POT/PS decreased from 10^{12} to $5.8 \times 10^9 \Omega$ when the molar ratio of DiOHP to POT was changed from 0.4 to 2, but they became almost a constant beyond the molar ratio of 2. Hence, POT chains are suggested to be in the expanded coil-like conformation at this molar ratio. It is worthwhile to note that the uniformity of the coating was not at all affected by the amount of DiOHP. This is

another advantage of the dip-coating method for the preparation of the conducting surface of ABS.

To check the surface uniformity and adherence of the coating on the ABS substrate, scanning electron micrographs of the ABS plates coated with DiOHP-doped POT and -doped PANI were measured, and the results are presented in Figure 6. It is known that triblock copolymers such as SBS and ABS exhibit a variety of morphological features depending on the composition and processing conditions.¹⁸ The ABS photograph obtained here shows a spongy-type fibrillar network with some voids [Fig. 6(a)]. The photograph of the ABS plate coated either with DiOHP-doped POT

[Fig. 6(b)] or -doped PANI [Fig. 6(c)] is unlike that of pure ABS. This indicates that the coated ABS is completely covered with the conducting material. The surface of the ABS plates coated with POT and PANI appear to be like silk cloth. The fibrillar strand with a smooth fold is still evident in the micrograph. The ABS plates coated with POT/PS and PANI/PS exhibited similar features.

The thermal characteristics of the polymers and coated ABS mentioned above were studied by TG/MS analysis. The thermal patterns of DiOHP-doped POT and -doped POT/PS are shown in Figure 7(a,b), respectively. The weight loss in the initial stage is attributed to the evaporation of *m*-cresol, which is either trapped in the polymer network or bounded strongly to the dopant and polymer chains. This is based on the fragments at *m/z* 107, 90, 79, 51, and 39 in the mass spectra recorded simultaneously with the thermal pattern [Fig. 7(a)-*t*₁]. The second stage comprising a 47.5% weight loss indicates the detachment of dopant anion from the polymer backbone. Several fragments with *m/z* 112, 83, 70, 55, and 41 are assigned to DiOHP [Fig. 7(a)-*t*₂]. Polymer chains from DiOHP-doped POT as well as its composite with PS can still withstand temperature *t*₂ (250°C) without undergoing decomposition or breakdown.⁴ Further heating the DiOHP-doped POT up to 400°C leads to the generation of various fragments (*m/z* 106, 93, 66, 77, 51) due to the polymer backbone [Fig. 7(a)-*t*₃]. On the other hand, for DiOHP-doped POT/PS, the third stage of decomposition extends up to 460°C, and fragments (*m/z* 51, 78, 65) originated from POT are clearly observed with those (*m/z* 104, 91, 78, 51) due to PS [Fig. 7(b)-*t*₁]. Higher weight loss at this step for DiOHP-doped POT/PS (55.7%) compared to that for DiOHP-doped POT (12.8%) suggests the complete degradation and decomposition of the PS backbone. Both polymers continue to degrade until 615°C, and at this temperature, the weight loss is entirely due to the generation of CO₂ [Fig. 7(a)-*t*₄]. The total weight loss was found to be 68 and 93.5% for DiOHP-doped POT and -doped POT/PS, respectively.

Additionally, the thermal patterns of ABS coated with DiOHP-doped POT and -doped POT/PS along that with pure ABS were measured to check whether there is any change in the thermal properties of ABS after being coated with the conducting polymer. Pure ABS showed a two-step decomposition pattern with a major breakdown occurring in the temperature region from 350 to 450°C (Fig. 8). From the mass spectra, it appears

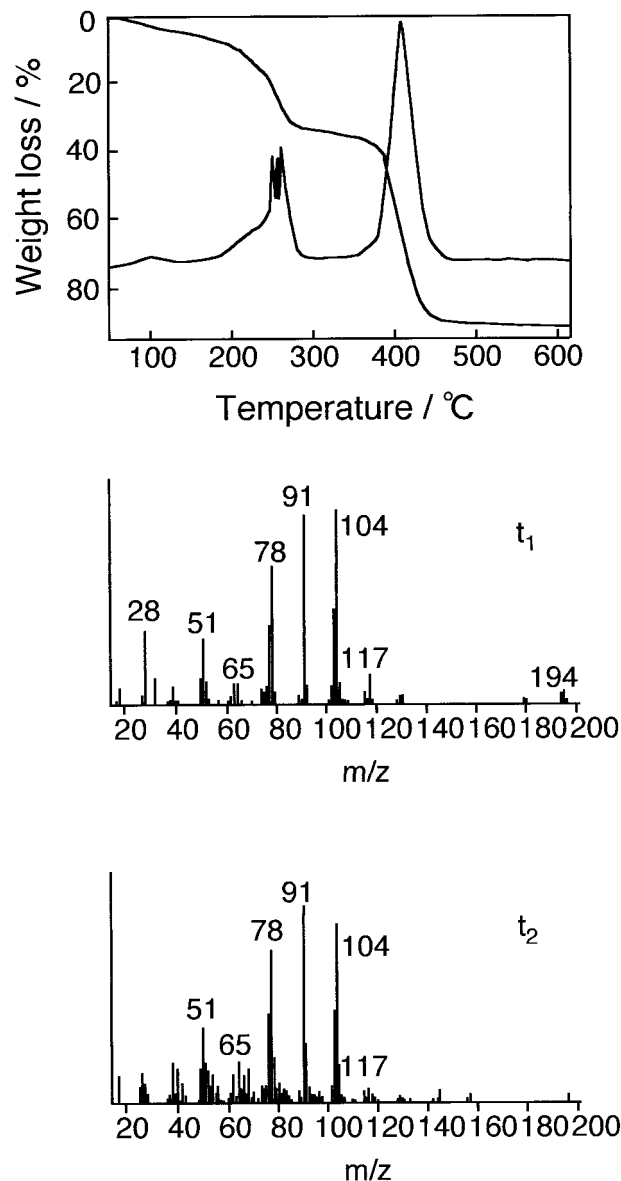


Figure 8 Thermal pattern of ABS recorded at the programmed heating scan rate of 5°C min⁻¹. Mass spectra were taken at *t*₁ 220 and *t*₂ 370°C.

that the weakening of the ABS matrix starts at 220°C (*m/z* 51, 78, 104, 120) (Fig. 8-*t*₁), whereas the mass spectra measured at 370°C reveal various fragments arising from a brisk breakdown and decomposition of ABS (Fig. 8-*t*₂).

Figure 9 represents the thermogram of the ABS plates coated with DiOHP-doped POT (a) and -doped POT/PS (b). The initial weight loss up to 220°C in both cases is attributed to strongly bounded *m*-cresol [Fig. 9(a)-*t*₁, *t*₂ and 9(b)-*t*₁, *t*₂]. Owing to very small amount of the coated material on ABS, the fragments due to dopant DiOHP

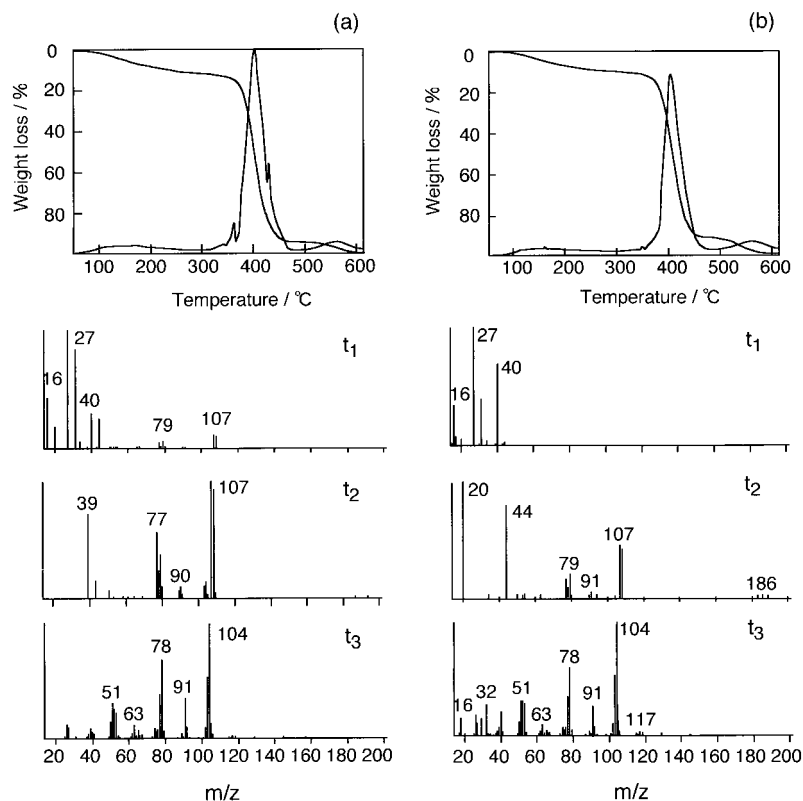


Figure 9 Thermal patterns of ABS coated with (a) DiOHP-doped POT and (b) DiOHP-doped POT/PS. Mass spectra were taken at t_1 130, t_2 220, and t_3 370°C.

were not visible in the mass spectra. On further elevation of the temperature up to 370°C, the ABS plates coated with DiOHP-doped POT and -doped POT/PS [Fig. 9(a)- t_3 , 9(b)- t_3] revealed similar fragments to that observed for pure ABS (Fig. 8- t_2), indicating that the coating is not affected by the underlying ABS [Fig. 9(a)- t_3 , 9(b)- t_3]. Additionally, the total weight loss of coated ABS was found to be 99.5%, while those of DiOHP-doped POT and -doped POT/PS films were 68 and 93.5%, respectively. The total weight loss of pure ABS was 99.5%, and it is suggested that the thermal property of the ABS matrix is not influenced by the overlying POT or POT/PS.

CONCLUSIONS

A simple dip-coating method was described for the preparation of the conducting surface of ABS. The ABS plates coated with DiOHP-doped PANI, -doped POT, and -doped PoAN possess surface resistivities of 3.0×10^5 , 2.4×10^7 , and 4.2×10^9 Ω , respectively. These values are low enough to

provide an antistatic surface of ABS, because, in general, the lowest surface resistivity in which ABS does not suffer from static charge buildup is about 10^{10} Ω . Although the coating containing PS was less conducting, PS contributed to the permanency and uniformity of the coating. The characteristics of the conducting polymer were found not to be altered drastically after coating on ABS, as evidenced by XRD, reduced viscosity, SEM, and TG/MS measurements.

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