Colloid & Polymer Science Colloid Polym Sci 272:244–250 (1994)

Original Contributions

Interaction of surfactant with antistatic polymer thin layers

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Abstract: Thin layers made from three kinds of hydrophilic polymer were coated onto poly(ethylene terephthalate)(PET) fibers to study the interaction of an anionic surfactant, sodium *n*-dodecyl benzenesulfonate, with the polymer layers. The coated layers include a) poly(vinyl alcohol) (PVA) crosslinked with glutaraldehyde [nonionic], b) crosslinked, sulfated PVA [anionic], and c) polyethyleneimine crosslinked with poly(ethyleneglycol diglycidylether) [cationic]. All of these coatings were found to reduce the electrostatic charging of the PET cloths, indicating that they were effectively coated with the hydrophilic polymers. The PET cloth coated with the thin layers was immersed in the aqueous solution of surfactant at 40 °C for different durations and the electrostatic voltage as well as the weight change were determined after drying. When the cloth coated with the nonionic or the anionic layer was brought into contact with the surfactant, neither the electrostatic voltage nor the weight of PET changed. On the contrary, immersion in the surfactant solution brought about an increase in both the electrostatic voltage and the weight for the PET coated with the cationic layer. This suggested that the surfactant molecules were bound to the cationic layer, in contrast to the nonionic and the anionic layer. It was concluded that the binding was due to ion complexing between the cationic groups in the polymeric layer and the sulfate groups in the surfactant molecules.

Key words: Surfactant – interaction – polycation – polyanion – polymer layers – antistatic – polymer coating– polymer interaction

Introduction

In the course of investigations on antistatic finishing of fabrics, we have found that the antistatic property often changes drastically when the fabrics coated with an antistatic layer are washed with surfactant solution. It seems probable that, when polymeric products such as fabrics, films, plastics are brought into contact with surfactant, adsorption or sorption of the surfactant molecules to the polymer surface or the interior will take place to some extent. The widely observed reduction in electrostatic voltage upon washing of cloths with the surfactant [1–3] may partly be related to the surfactant interaction with the fibers. Although extensive studies have been carried out for the interaction of ions with soluble polymers [4–7], only a few have been devoted to the interaction with polymers in a solid or swollen state [8–10].

The present work was undertaken to study the surfactant interaction with polymeric thin layers coated on a substrate. To this end, three kinds of thin layers, that is, nonionic, anionic, and cationic layers were coated to poly(ethylene terephthalate) (PET) fibers. We will study the surfactant interaction by determining the change in electrostatic voltage and weight of the PET substrate coated with the thin layers after being brought into contact with the surfactant.

Experimental

1. Cloth

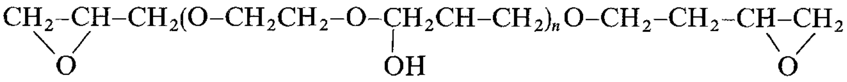
The PET cloth employed was plainly woven with bulky yarns from multifilaments consisting of 48 monofilaments of 3 denier. The density of cloth was 60 yarns/in both for the longitudinal and the latitudinal direction. The cloth was cut to 5 × 5 cm and cleansed by immersing in water and then methanol, each, for 50 h at room temperature.

2. Coating

Nonionic coating: The cleansed cloth was dipped in a 1.0 wt % aqueous solution of poly(vinyl alcohol) (PVA) containing glutaraldehyde (GA) and 0.05 N HCl. The viscosity-average molecular weight of PVA was 7.5×10^4 and the GA concentration was 1.0 mol % of the PVA repeating unit. After pressing the imbibed cloth between two filter papers so as to have a desired pick-up deposit, it was heated for 30 min in an oven kept at 105 °C to allow acetal crosslinking of PVA with GA to proceed and then washed with distilled water at 50 °C for 30 min.

Anionic coating: The cloth coated with the crosslinked PVA layer was put in a mixture of sulfation consisting of chlorsulfonic acid and pyridine (1:4 by volume) and kept for 3 h at 65°. After that, it was neutralized with 0.05 N Na_2CO_3 and then washed with water at room temperature for 5 min.

Cationic coating: The cleansed cloth was dipped at room temperature in aqueous solution containing poly(ethylene imine) (PEI) and an oligomer of ethyleneglycol diglycidylether(PEGDE) at different ratios. The number-average molecular weight of PEI was 7×10^4 and the molar ratio of primary, secondary, and tertiary amine was 1:2:1. PEGDE has the following chemical structure:



$$\underset{\diagdown O \diagup}{CH_2-CH}-CH_2(O-CH_2CH_2-O-\underset{OH}{\underset{|}{C}}H_2CH-CH_2)_nO-CH_2-CH_2-\underset{\diagdown O \diagup}{CH-CH_2}$$

The *n* value of PEGDE used in this work distributed from 0 to 4, but was mostly around zero. pH of the dipping solution and the solution concentration of PEI were adjusted to 7 with HCl and 2.5 ± 0.5 g/dl, respectively. After the cloth imbibed with the reaction mixture was squeezed to give pick-up deposits, it was heated at 105 °C for 30 min. For removal of reactants eventually remaining unreacted inside the coated layer, the coated cloth was washed with water and then dried.

3. Contacting with surfactant

The coated cloth was brought into contact with the surfactant at 40 °C by immersing it in the surfactant solution with a concentration of 0.13 g/dl. The surfactant employed was sodium *n*-dodecyl benzenesulfonate of analytical grade and was used as received. The cloth was vibrated, while the surfactant solution was at the same time stirred. In some cases this procedure was performed intermittently in such a way that the cloth was immersed in the surfactant solution for a given duration, dried, and then immersed again in the surfactant solution.

4. Measurement of electrostatic voltage and wicking time

The cloth was charged at 55 ± 2% RH and 21 ± 1 °C using a Rotary Static Tester developed at the Institute for Chemical Research, Kyoto University, and manufactured by Koa Shokai, Ltd., Japan. The measurement of electrostatic voltage of the charged cloth with this instrument was carried out as follows [11]. In order to give an electrostatic charge to the cloth, it was rubbed with a reference cotton cloth fixed on a cylinder rotating at a speed of 500 rpm. The electrostatic voltage of the charged cloth was read after rubbing for 1 min. Mostly, saturation of the electrostatic charging was reached within about 0.5 min after rubbing. The wicking time of cloth was determined by putting a water droplet of 0.3 ml from a tip of burette on the cloth surface which was placed 2 cm below the burette tip. The duration necessary for the droplet to be completely imbibed in the cloth was recorded as the wicking time.

Results

1. Electrostatic charging.

1.1. Nonionic and anionic layers. Figure 1 shows the electrostatic voltage of the noncoated and the coated PET cloth which has been brought into

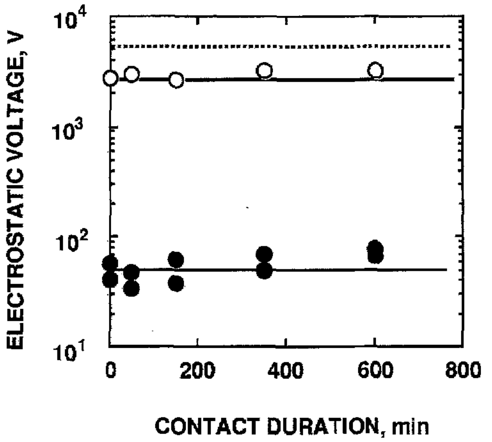


Fig. 1. Electrostatic voltage of PET coated with nonionic and anionic polymers as a function of duration of contact with surfactant. (○) nonionic coating with PVA at 1.0 mol % GA and a deposit of 1.5 wt %; (●) anionic coating with sulfated PVA; (---) noncoated PET

contact with the surfactant solution for different periods of time. The coated polymers are a crosslinked PVA (nonionic) and a crosslinked, sulfated PVA (anionic). The deposit of coated PVA is 1.5 wt %. Throughout this work, the polymer deposit was expressed on the basis of the weight of starting cloth. As can be seen from Fig. 1, the noncoated PET has an electrostatic voltage as high as 6000 V, whereas the voltage is reduced to 2800 and 60 V by coating with PVA and further by introducing sulfate groups to the PVA, respectively. In addition, it should be noted that the electrostatic voltage remains in every case nearly constant, regardless of the duration of contacting with the surfactant solution. This indicates that the coated polymer layers are fixed strongly enough not to be peeled off from the PET surface even when immersed in the surfactant solution.

As is clear from Fig. 1, no significant difference in electrostatic voltage is seen between before and after contacting with the surfactant solution. This implies that surfactant adsorption or sorption to the virgin PET, the PVA, and the sulfated PVA is not taking place, or is very weak if at all.

1.2. Cationic layer. In a preliminary experiment, the optimum pH for crosslinking of PEI through the reaction of amino groups of PEI with epoxides attached to the chain ends of PEGDE was found to be in the vicinity of 7. If the temperature for crosslinking was in the range from 70° to 130 °C and the pH of the reaction mixture was kept at 7, the coated layer became insoluble within about 30 min, independent of the ratio of PEI to PEGDE. Figure 2 shows the effect of the PEI fraction in the PEI-PEGDE mixtures on the electrostatic voltage. The polymer coating was carried out at a deposit of 1.5 wt %. Not only the ionic density but also the crosslink density in the coated layer must vary with the PEI fraction. It is seen from the inserted figure in Fig. 2 that low fractions of PEGDE, such as 0.01–0.02, are sufficient for the crosslinking of PEI. When PEI was applied for coating without PEGDE, the electrostatic voltage of the coated surface recovered almost to that of the virgin PET upon washing with water. This clearly indicates that the PEI molecules are undoubtedly crosslinked by the help of PEGDE. Also, a coating of only PEGDE could be readily stripped off by washing with water. It is likely that the minimum present in the curves in Fig. 2(b) is a consequence of compromise between the indispensable crosslinking of PEI with PEGDE and less hydrophilicity of PEGDE crosslinker than PEI. It can also be seen in Fig. 2 that the electrostatic voltage of the coated surface increases as the duration of its contacting with the surfactant solution becomes longer.

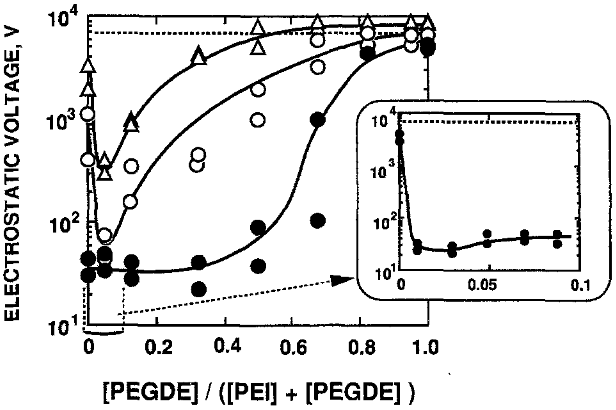


Fig. 2. Dependence of electrostatic voltage on the composition of cationic layer coated on PET at a deposit of 1.5 wt %. (●) after washing with water for 50 min; (○) after contacting with surfactant for 50 min; (△) after further contacting with surfactant for 100 min; (– – –) noncoated PET

The effect of surfactant treatment on the electrostatic voltage of the cationic layer is given in more detail in Fig. 3. The coating was performed at a PEI fraction of 0.95 and a deposit of 1.5 wt %.

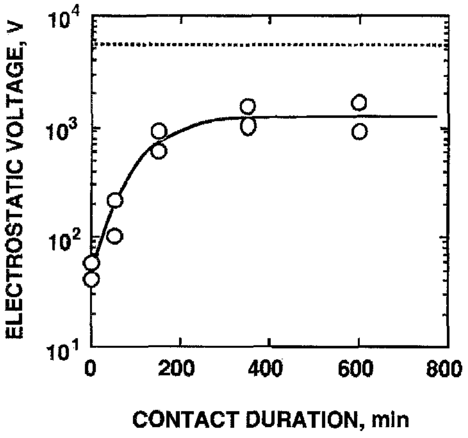


Fig. 3. Electrostatic voltage of PET coated with cationic polymer as a function of duration of contact with surfactant. (○) cationic coating at a deposit of 1.5 wt % and [PEI]/([PEI] + [PEGDE]) of 0.95; (---) noncoating

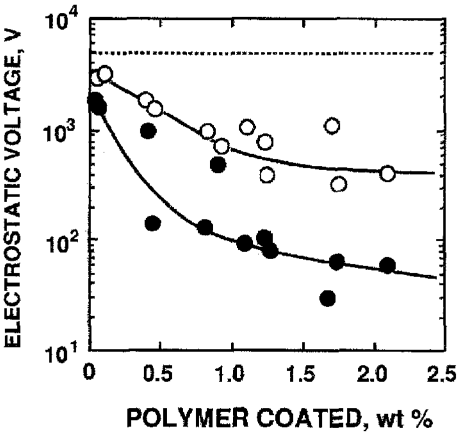


Fig. 4. Dependence of electrostatic voltage on the deposit of polymer coated on PET at a [PEI]/([PEI] + [PEGDE]) of 0.95. (●) after washing with water for 100 min; (○) after contacting with surfactant for 130 min; (---) noncoated PET

As can be seen in Fig. 3, the coated layers had very low electrostatic voltages such as several tens of volts if not brought into contact with the surfactant. Washing with pure water did not enhance the lowered electrostatic voltage, but it again increased with the increasing duration of contact with the surfactant solution approaching a saturated value, which was, however, clearly lower than the electrostatic voltage of the virgin PET. Figure 4 demonstrates the effect of the deposit on the electrostatic voltage for the layer coated at a PEI fraction of 0.95. Apparently, 1 to 2 wt % deposit is not yet sufficient to reduce the electrostatic voltage to a leveling-off value. Also in this case, the surfactant effect was obviously noticed.

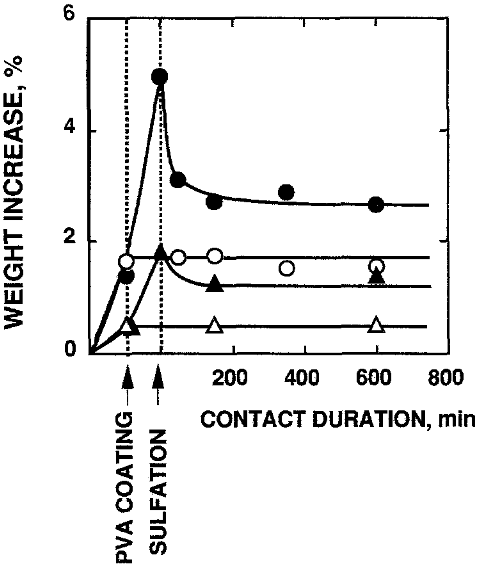


Fig. 5. Weight increase of PET after coating with PVA at 1.0 mole % GA, subsequent sulfation, and contacting with surfactant. (●, ○) coated with PVA at a deposit of 1.5 wt %; (▲, △) coated with PVA at a deposit of 0.5 wt %. Open marks (○, △) indicate the result without sulfation

2. Surfactant binding

2.1. Nonionic and anionic layers. Figure 5 shows the weight change of the PVA-coated layer observed when it has been immersed in the surfactant solution and then dried. The result for the PVA coating followed by sulfation is also given in Fig. 5. In both cases, the weight increase, expressed in %, is based on the weight of the starting PET. As is clearly seen, contacting with the surfactant solution brings about no additional weight change for the nonionic PVA coated layer. On the other hand, a slight weight decrease is observed for the layer coated with the sulfated PVA, when treated with the surfactant solution. It seems likely that by-products or reactants of sulfation, included eventually in the layer, can be poorly extracted with water, but much more effectively with the surfactant solution. Together with the result shown in Fig. 1, no further weight change by the surfactant treatment, neither for the PVA nor the sulfated PVA layer, also confirms the insignificant interaction of the surfactant with the nonionic and the anionic surface.

We can estimate the degree of sulfation from the result given in Fig. 5 under the assumption that no surfactant molecule is sorbed to the layer, whereas only the coated PVA and the sulfate groups introduced to the PVA are responsible for the weight increase. The estimated degrees of sulfation are 51 and 73%, which are approximately equal to the values to be expected when a noncrosslinked, conventional PVA is subjected to sulfation under a similar reaction condition.

2.2. Cationic layer. The weight change observed for the cationic layer when immersed in the surfactant solution is represented in Fig. 6, where the result of simple water washing is also given. The deposit described throughout this work is the weight increase after this water washing. It is seen from Fig. 6 that the weight decreases upon washing with water, but again increases as a result of contacting with the surfactant solution. There is no reason to suspect that the first decrease in weight with the water washing is due to removal of some compounds remaining unreacted. In contrast with the anionic coating, a considerable weight increase is observed for all the cationic coatings when brought into contact with the surfactant solution. Obviously, this weight increase is ascribed to binding of the surfactant molecules to the cationic layer. This binding is not a result of adsorption to the surface of the coated layer, but mostly sorption of the surfactant molecules to the inside of the coated layer. Such a high weight increase, of a few weight percent, is improbable if the binding is restricted to the surface of coated layer alone.

From the result given in Fig. 6, one can calculate the weight of the surfactant bound to the coated layer. The calculated weight is plotted as a function of the deposit in Fig. 7. The results for coating with PEI of other fractions are also given in Fig. 7. It is clearly seen that the weight of

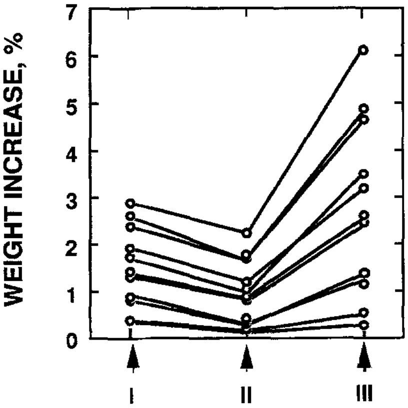


Fig. 6. Weight increase of PET after coating with cationic layer at various deposits and a fixed [PEI]/([PEI] + [PEGDE]) of 0.95 after washing with water and further contacting with surfactant. (I) as coated; (II) after washing with water for 50 min; (III) after further contacting with surfactant for 150 min

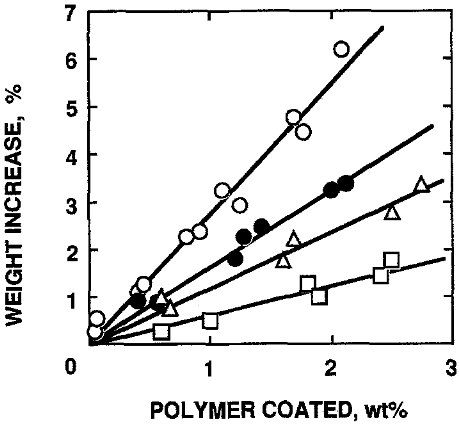


Fig. 7. Weight increase of PET coated with cationic layer after contacting with surfactant for 150 min as a function of the deposit of polymer coated. (□) [PEI]/([PEI] + [PEGDE]) = 0.27; (△) [PEI]/([PEI] + [PEGDE]) = 0.50; (●) [PEI]/([PEI] + [PEGDE]) = 0.67; (○) [PEI]/([PEI] + [PEGDE]) = 0.95

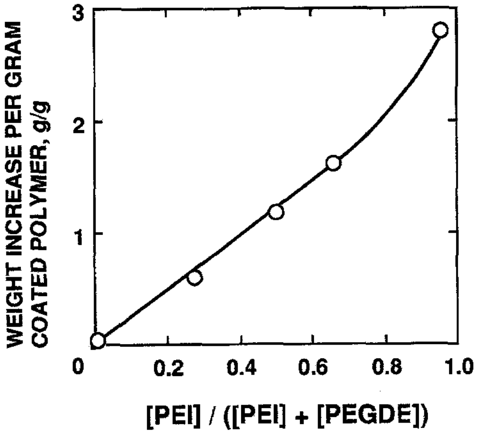


Fig. 8. Weight increase per gram of coated cationic polymer after contacting with surfactant for 150 min as a function of the composition of coated polymer

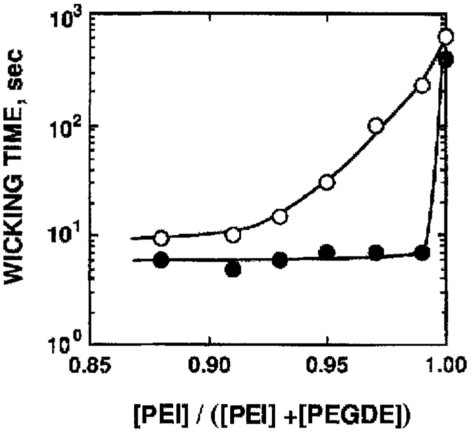


Fig. 9. Wicking time of PET coated with cationic layer at a deposit of 1.5 wt % before and after contacting with surfactant as a function of the composition of coated polymer. (●) before and (○) after contacting with surfactant for 50 min

surfactant bound per 100 g of coated cloth linearly increases in every case with the increasing deposit. This again confirms that the surfactant binding is occurring not through adsorption but sorption, because surfactant weight is proportional to the weight of the coated layer, not to the total surface area of the coated layer.

As is seen from Fig. 8, where the slope of the straight lines in Fig. 7, that is, the surfactant weight per gram of deposited layer is plotted against the fraction of PEI in the layer, the weight of bound surfactant becomes higher as the PEI content in the coated layer is larger. The proportionality seen at least in the low PEI fraction range means that the surfactant does not interact with PEGDE moiety but directly with PEI. The number of surfactant molecules per PEI monomer unit is estimated from the initial slope of the curve in Fig. 8 to be approximately 0.3. For comparison, the dependence of the PEI content on the wicking time is shown in Fig. 9. The wicking time can be regarded as a measure of hydrophilicity of the cloth, because it is closely related to water accessibility to the cloth. It can be seen that the dependence on the PEI content becomes much remarkable when the surfactant is bound to the layer.

Discussion

Since PET itself is apt to be electrostatically charged in contrast with hydrophilic polymers, one can readily recognize whether or not any hydrophilic polymer is covered on the PET surface. In the present study, it is necessary for the coated layer to not be readily peeled off from the substrate when brought into contact with water, the reaction mixtures, or the surfactant solution. None of the results described above shows any tendency of peeling-off for the coated layer.

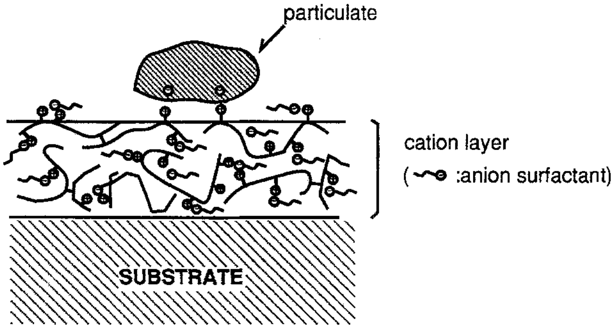


Fig. 10. Schematic representation for ion complexing between anionic surfactant molecules and the cationic layer coated on a polymer substrate. Attaching of a particulate to the surface is also depicted

As is obvious from Figs. 1 and 5, the surfactant seems to not interact with the PVA thin layer, so far as can be judged from its effect on the electrostatic charging and weight change. Figures 1 and 5 further demonstrate that the interaction of the surfactant with the anionic layer which was produced by sulfation of the crosslinked PVA layer is insignificant. Marked reduction in electrostatic voltage and weight increase are caused by the introduction of the cationically charged groups. It is interesting to point out that the PVA coating alone does not reduce the electrostatic voltage to a significant extent in comparison with the polyanion coating, though PVA is regarded as a typical hydrophilic polymer.

Contrary to coating with the nonionic PVA and the anionic sulfated PVA layer, coating with PEI and PEGDE mixtures leads to an increase in electrostatic charging and weight, indicating the binding of the surfactant molecules to the cationic layer. It is highly probable that this binding is of electrostatic nature, since only the cationic layer is affected by the surfactant treatment and the surfactant employed in this work is anionic. One strong support for the ion complexing is provided by the result given in Fig. 8. It is seen that the surfactant binding takes place more strongly as

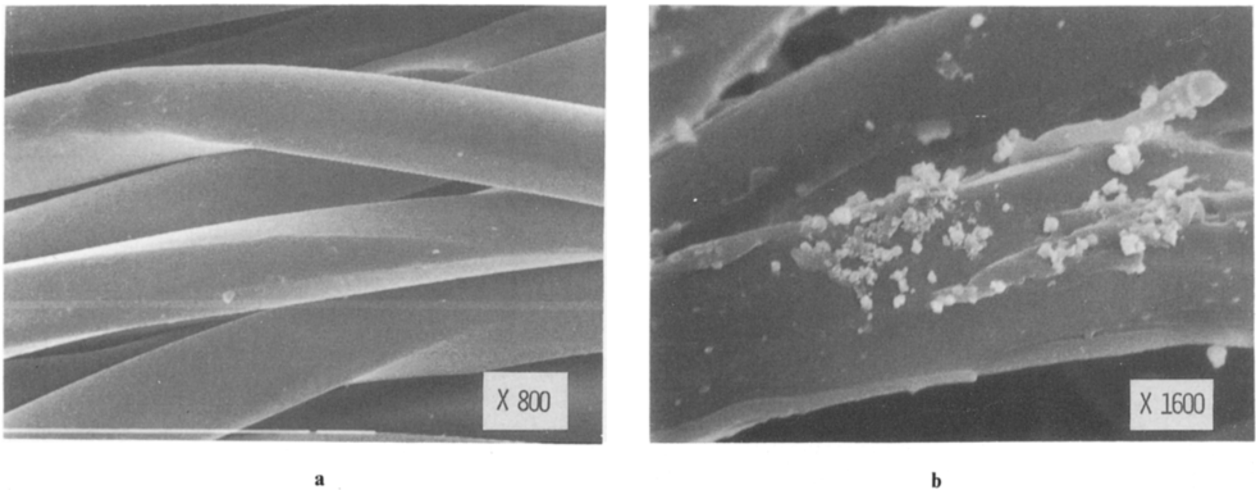


Fig. 11. SEM photographs of PET fibers coated with cationic layer at a deposit of 1.5 wt % and [PEI]/([PEI] + [PEGDE]) of 0.95. (a) before and (b) after contacting with surfactant for 150 min

the PEI content in the layer becomes higher. In addition, the ion complexing is supported by the influence of PEI content on the wicking time. As shown in Fig. 9, the difference in wicking time between before and after surfactant binding is less prominent as the PEI content decreases, probably because the hydrophilic moiety which strongly affects the wicking disappeared as a result of complexing with the anionic surfactant. Deviation from the linearity seen is Fig. 8 is probably due to attachment of substances other than the surfactant molecules.

The surfactant binding through ion complexing is depicted schematically in Fig. 10. Attachment of a small particulate on the layer surface is based on scanning electron microscopic photographs. One example is shown in Fig. 11. As is apparent, the PET fibers coated with the cationic layer have a clean and smooth surface unless they come in contact with the surfactant solution, whereas small particulates attach to the surface when it is allowed to contact with the surfactant solution. Sello and Stevens also pointed out that the cationic surface can be readily contaminated [12]. One cannot exclude, however, the possibility of hydrophobic interaction between the coated layer and the surfactant or particulate.

In conclusion, it may be summarized that sodium *n*-dodecyl benzenesulfonate, an anionic surfactant, can almost quantitatively bind to the cationic moiety existing in the thin layer coated on a polymer substrate, while the anionic layer covering the substrate does not interact with the surfactant at all, leading to at least triboelectrification and excellent durability against cleansing with surfactant.

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Received December 11, 1992;
accepted June 22, 1992

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