Electrostatic Properties of UV-Irradiated and Surface-Grafted Polymers

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Synopsis

A polystyrene film, a poly(ethylene terephthalate) (PET) film, and PET fabrics were UV-irradiated or surface-grafted with various hydrophilic monomers. Their electrostatic properties were studied by measuring the triboelectric charges generated upon mechanical rubbing of these materials and by following the decay of the charges generated upon exposing the polymeric materials to a high electric field. The UV-irradiated polymers carried lower electrostatic charges than those unirradiated after their surfaces were rubbed with a cotton fabrics under the same conditions. The generation of triboelectric charge depends on both the surface hydrophilicity and the past history of the specimens. Although hydrophilic groups introduced on the polymer surface by UV exposure exhibited little effect on decaying of the electrostatic charge, polymeric materials grafted with a large amount of water-soluble polymers, especially with ionic polymers, showed lower triboelectric generation and faster decay of the static charge.

INTRODUCTION

The generation of electrostatic charges on polymers has been mostly a nuisance in many fields associated with polymer and textile technologies. In addition to discomfort from static cling or static discharge, it often causes serious damage in semiconductor manufacture and sometimes to human life through fire or explosion. Therefore, it would be of great value to devise a simple method for eliminating static generation during the manufacturing process or to develop a new polymer that prevents charge generation. The mechanism for generation of the triboelectric charge is still controversial and it remains unclear whether the electric charge carrier is electrons, ions, or both. According to Montgomery and Loeb, the carrier might be electrons,[1,2] whereas Harper maintains that the carrier is not entirely electrons if the charged material is strictly an insulator.[3] Whatever the mechanisms of charge generation are in equilibrium processes, it is possible to arrange materials in an electrostatic series such that any material in the series will become positively charged when brought into contact or rubbed with another material below it in the series.[4,5] According to Shaw and Hanstock,[6] triboelectric charging is greatly influenced by the manner of rubbing. For instance, when quartz is rubbed hard with a silk it becomes positive, whereas it becomes negative when brushed lightly with the silk. When similar pieces of an insulating material are rubbed together and the rubbing is inevitably asymmetric, there can be positive or negative charges, depending on the effect of

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friction on the two solid surfaces.[7] Henry[8] emphasized the importance of the temperature rise during rubbing, because the charge carrier would become easier to transport from one surface to the other at high temperatures. Lowell and Truscott[9] studied the dependence of triboelectric generation on the friction speed. The higher the speed, the higher the temperature should become. However, contrary to Henry's observation, nylon and polytetrafluoroethylene were little influenced by the friction speed. It follows that the triboelectric charge generated on a polymer surface upon contacting or rubbing with another material cannot be identified absolutely. In addition, it should be noted that the charge is very unstable and depends on a variety of factors. For instance, the atmospheric conditions such as temperature and humidity will play a great role in the electrification of a surface.[10] As suggested above, both the magnitude and the sign of the electrostatic charge depend on the species of the opposing substrates, the pressure at contacting and rubbing, contaminants, the past history of the specimen, and so forth.[11-14]

Regardless of the source, static charge is readily produced on polymeric materials having high electrical resistances when they are brought in contact with other solid surfaces, followed by separation or when they are placed in a high electric field. It is often difficult to dissipate their charges rapidly. Even highly conductive metals can be electrified under the same condition as polymeric materials, although their charge diminishes instantaneously if grounded. Many efforts have been made to minimize the electrostatic charging, mostly by rendering the polymer surfaces hydrophilic or electroconductive. The methods employed include surfactant mixing and metal fiber coweaving. Surface modifications of polymeric materials have been also studied in an attempt to reduce the generation of electrostatic charges.[15-17] We have already reported the surface modification of polymers through grafting with the use of glow discharge,[18] corona discharge,[19] and irradiation with ionizing[20] and UV radiations.[21] The purpose of the present work is to study the electrostatic charging of surface-treated polymers. To this end, polystyrene and poly(ethylene terephthalate) films were irradiated with UV radiation and further surface-grafted with hydrophilic monomers. The electrostatic properties of these UV-irradiated and surface-grafted polymers were studied by charging through mechanical rubbing or exposure to high electric fields.

EXPERIMENTAL

Materials, UV Irradiation, and Graft Polymerization

Films of commercial grade polystyrene (PS) and poly(ethylene terephthalate) (PET) were prepared with a thickness around 30 μm. The films with a size of 5 $\times$ 5 cm^2 were purified by Soxhlet extraction with methyl alcohol for 20 h and then dried under reduced pressure. The purified films were stored in a desiccator kept at 25°C and 60% RH, being placed between two filter papers. Fabrics of cotton and PET were used as received without purification.

UV irradiation of the films was performed with a high-pressure mercury lamp (75 W, Toshiba SHL-100UV type, $\lambda > 254$ nm) in air at room temperature by placing them 7 cm from the center of the light source.

The surface graft polymerization of various water-soluble monomers onto the PS and PET films and the PET fabrics was conducted according to the method described elsewhere.[22] Briefly, a quartz glass tube containing the aqueous monomer solution in which the films or fabrics was immersed was irradiated with UV. The ungrafted homopolymer was extracted with boiling water.

Electrostatic Measurements

Triboelectric charges were generated on the polymeric materials and measured at 25°C and 60% RH using a Rotary Static Tester (Kyodai Kaken type, Koa Shokai Ltd., Kyoto, Japan) by relatively gentle rubbing with the cotton fabrics for 30 s unless noted, because excessive rubbing might spoil the surface of the tested polymeric materials. The structure of the apparatus used is schematically illustrated in Figure 1. The test specimen (A) is fixed on a drum (B), which rotates at a rate of 540 rpm. As the diameter of the drum is 20 cm, the number of rubbings with the cotton fabrics (C) is 540/min at a rate of 565 cm/s. The test specimen comes downwards on rotation and in contact with the cotton fabrics. The triboelectric charge generated is measured with a detector (D). A constant tension is applied to the cotton fabrics with a 500-g load (E). No significant difference in triboelectric charge was observed between the original cotton fabrics and the fabrics used after Soxhlet extraction with methanol. This indicates that there is no significant finish. To make measurements under the same conditions, the cotton to be used for rubbing was always replaced with a fresh one.

The rate of electrostatic decay was determined by measuring the half decay time, τ, of test specimens, which were initially charged to +5 kV or −5 kV by corona discharge, at 20°C and 75% RH using a Static Honestmeter (Shishido Shokai Ltd., Tokyo, Japan). When it took too much time to determine the τ value, the percent of electrostatic charge still remaining after 3 min was determined.
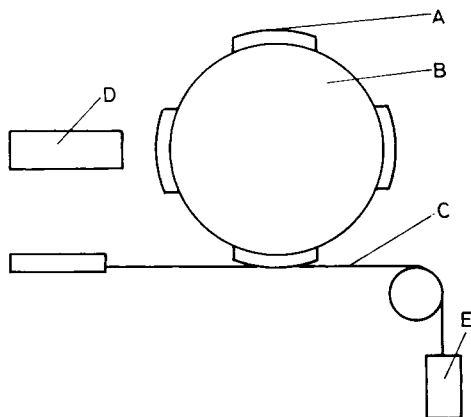

Fig. 1.   Schematic representation of the apparatus used for determining the triboelectric charge generated upon rubbing with a cotton fabrics: A, specimen; B, rotary drum; C, cotton fabrics; D, detector; E, load.

RESULTS AND DISCUSSION

Unirradiated Films

As mentioned earlier, there are many complicating factors that influence the absolute value of a triboelectric charge generated on polymer surfaces. To minimize these complexities, it is necessary to measure the triboelectric charge of polymers under conditions as identical as possible for every measurement. The triboelectric charge generated on the unirradiated PS film is plotted against rubbing time in Figure 2, together with that for the PS film that had already undergone intermittent rubbing five times (a 30-s rubbing every 1 h). As can be seen, the triboelectric charge of film that has experienced rubbing is much greater than that for the freshly prepared starting film, reaching about −6 kV, although the rate of generation of triboelectric charge is almost the same for both films. However, it should be noted that the virgin PS film did not show any charge greater than −5 kV when rubbed continuously for 3 min, which corresponded to 3 s × 6 times. This may be due to temperature rise during
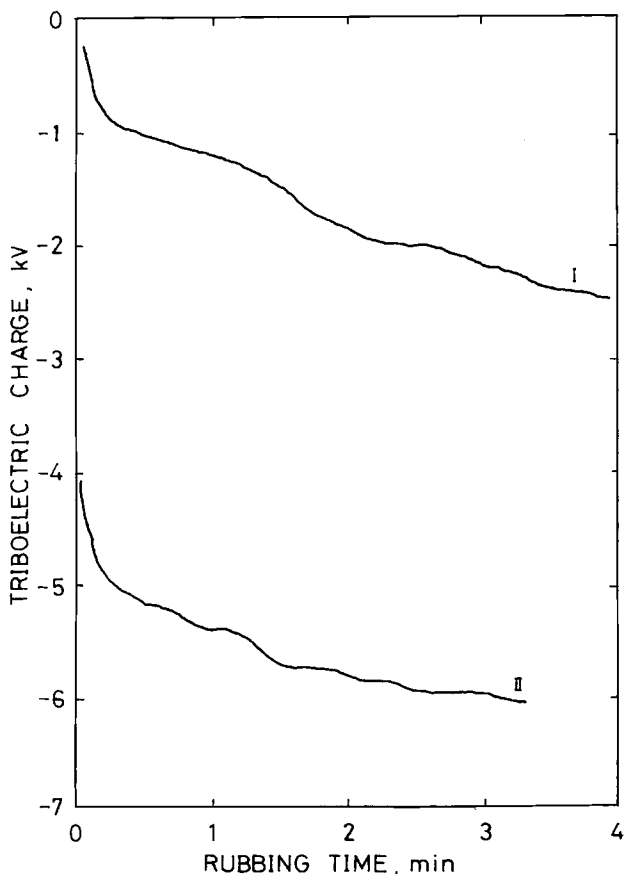

Fig. 2.   Triboelectric charge generated upon rubbing a polystyrene film with a cotton fabric: I, without any previous rubbing; II, after rubbing 5 times, each for 30 s.

continuous rubbing, because heating may make it easy for the charge carrier to transfer from the surface to the bulk or to the grounded equipment, resulting in a smaller amount of storage of electrostatic charge. This assumption is also supported by the fact that the triboelectric charge was always reduced when the contacting area of film and cotton fabrics was heated with an electric heater during rubbing. Watson[23] also studied the decay of surface electrostatic potential of a PS film at temperatures above and below the glass transition temperature (Tg). He concluded that, in the process of the transport of electrons from the surface into the bulk of PS, the decay is closely associated with the electron mobility and segmental motion in the rubber-like PS at temperatures above Tg. Below Tg, he concluded that the electrons remain frozen in traps in the polymer for an extremely long time. It is well known that polymer insulators such as PS retain their surface potential for a long period of time.

Figure 3 shows the result for the PET films. As can be seen, the difference in generated charge between the virgin and the rubbed films is much smaller than for the PS films. The rate of charge generation is also different. We do not have any clear explanation for this, but it seems likely that the relatively high hydrophilicity of PET will promote discharging of accumulated charge carriers more than the less hydrophilic PS. The contact angle of the virgin PET film against water is 64°, while that of the virgin PS film is 87°.

UV-Irradiated Films

In general, polymer surfaces undergo oxidation upon UV irradiation, resulting in more hydrophilic surfaces due to the generated polar groups. Figure 4 gives the O_{1S}/C_{1S} ratio obtained by an ESCA study for the films' surfaces, together with their water contact angles. It is seen that UV irradiation oxidizes the surface of PS and PET films, resulting in reduced water contact angles. Ap-
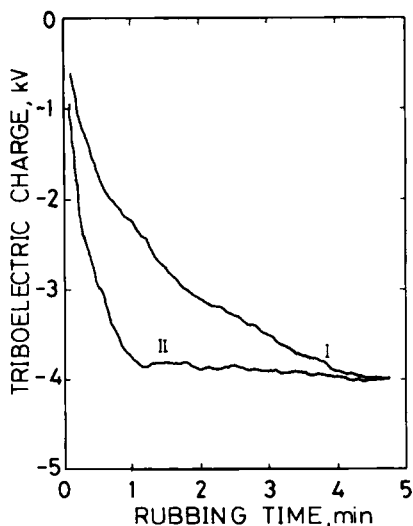

Fig. 3.   Triboelectric charge generated upon rubbing a poly(ethylene terephthalate) film with a cotton fabric: I, without any previous rubbing; II, after rubbing 5 times, each for 30 s.
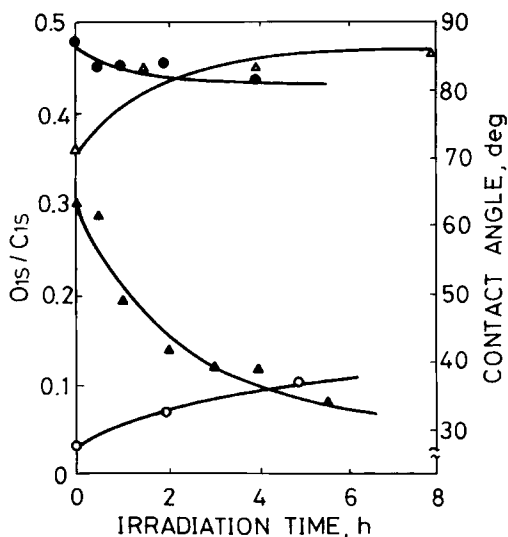
Fig. 4. Variation of O_{1s}/C_{1s} intensity ratio (open marks) and water contact angle (filled marks) as a function of UV irradiation: $\bigcirc$, $\bullet$, polystyrene; $\triangle$, $\blacktriangle$, poly(ethylene terephthalate).

parently, the PET film is more strongly oxidized by UV irradiation, as the reduction of contact angle takes place more markedly for the PET film than for the PS film.

The triboelectric charge generated on the UV-irradiated PS films upon rubbing is shown in Figure 5. The virgin and the UV-irradiated PS films were first rubbed only for 30 s. For the UV-irradiated PS films in particular, continued rubbing for longer periods of time was avoided because the surface suffered erosion by excessive rubbing. As described earlier, the density of the polar groups introduced on the surface of PS film by UV irradiation seemed low compared with PET film. Actually, the surface of UV-irradiated PS film lost its hydrophilic character when rubbed repeatedly for periods longer than 30 min, suggesting that oxidation was limited to the surface region. The tested films were kept at 25°C and 60% RH for 1 h and measurement was made in the same manner as for the first one after rubbing for 30 s. The previously rubbed films were further repeatedly rubbed for 30 s, after being kept for 2 h, 5 h, and 2 days after UV irradiation and the generated charge was measured. As is represented in Figure 5, the triboelectric charge apparently varied in a peculiar way with the increasing UV irradiation time. The films irradiated for 1 and 2 h seem to be more susceptible to triboelectrification than either the unirradiated film or films irradiated for longer than 2 h. However, as can be seen in Figure 5, the difference in the static charge between each step of rubbing is large for the unirradiated film and films irradiated for 1 to 2 h, whereas UV irradiation for longer than 3 h induces an insignificant charge difference between each rubbing step. This may be attributed to the different times to reach the maximal charge between the unirradiated and the UV-irradiated films. Sereda and Feldman[24] studied charging of various fabrics by rolling them between a nickel-plated roller and a nickel plate and found that the electrostatic charging on the fabric materials increased with the number of passes of the roller until
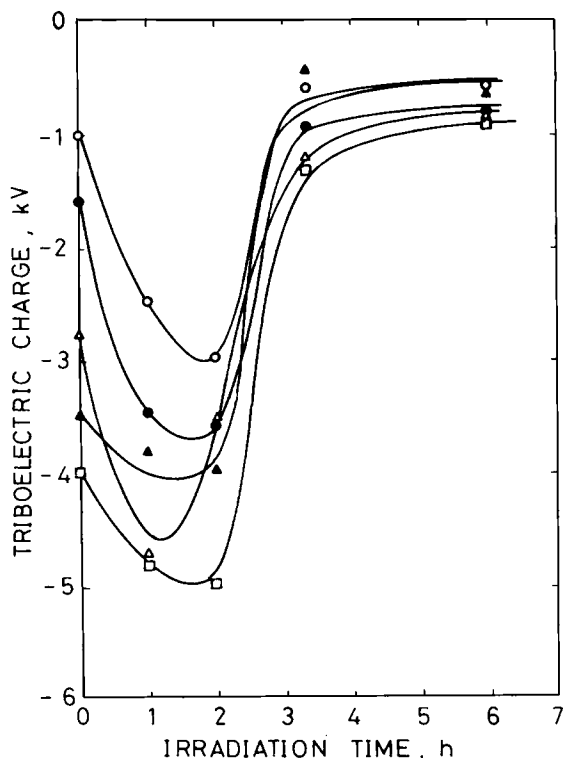
Fig. 5.   Triboelectric charge generated upon rubbing UV-irradiated polystyrene films with a cotton fabric at 25°C and 60% RH: O, measured immediately after UV irradiation; ●, 2nd after 1 h; △, 3rd after 2 h; ▲, 4th after 5 h; □, 5th after 2 days.

it reached a maximum, and that the maximal charging was quickly achieved at higher relative humidity with formation of a monomolecular layer of water on the surface of materials. Referring to their results, the finding in Figure 5 may be explained as follows: the maximal charging is more readily reached when the surface becomes more hydrophilic by UV irradiation for 1 or 2 h, although the amount of hydrophilic groups introduced must be small, as expected from Figure 4.

For the UV-irradiated PET films, rubbing was conducted not intermittently but continuously because the maximum charging could be easily obtained, as can be seen from Figure 3, and no significant erosion of polar groups was observed for the UV-irradiated PET films.

The maximum charge generated on the UV-irradiated PS film after a sixth intermittent rubbing is plotted in Figure 6, together with that of the UV-irradiated PET film, which was rubbed only once continuously for 3 min. As is clear, the maximal triboelectric charge is reduced with the increasing irradiation time for both films. Comparison of Figure 6 with Figure 5 shows that repeated rubbing of the PS film further promotes the accumulation of electric charge.

However, it does not mean that the PS and PET films acquired improved properties as antistatic material by UV irradiation, because a low level of hydrophilic groups introduced by UV irradiation does not render the polymer
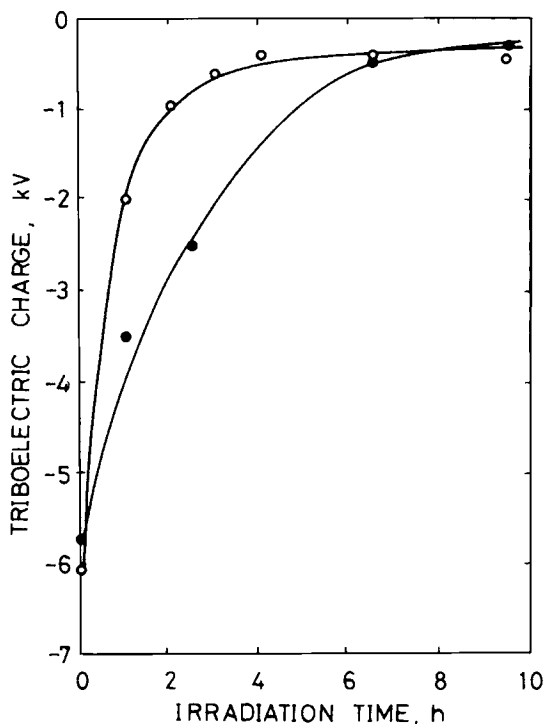
Fig. 6.   Maximum triboelectric charge of UV-irradiated (O) polystyrene and (●) poly(ethylene terephthalate) films as a function of irradiation time.

surface conductive at all. Moreover, the UV-irradiated films did not exhibit any significant reduction in decay time of static charge, as is shown in Table I. The electrostatic charge generated by corona discharge did not decay to the half value even after 1 h. Only 2.7% of the charge disappeared after 3 min for the PS film irradiated for 5 h, although the initial charge was as low as −0.9 kV.

Surface-Grafted Materials

Most industrial films, plastics, and rubbers are hydrophobic and readily charged by rubbing. Since less hydrophobic materials are generally more difficult to charge, it seems interesting to study triboelectric charging of hydrophobic polymeric materials whose surface is grafted with hydrophilic polymer chains. To examine the triboelectrostatic property of a hydrophilic polymer, a film of crosslinked poly(N,N-dimethylacrylamide) (PDMAA) was prepared by thermal polymerization of DMAA in the presence of a small amount of methylene bis-acrylamide as a crosslinking agent. The triboelectric charge of the obtained PDMAA film was dependent on the storage condition. When the film was thoroughly dried under a reduced pressure of about 0.1 torr prior to the charge measurement, the triboelectric charge was +0.9 kV, whereas film stored at 25°C and 60% RH for at least 1 week exhibited +0.02 kV as the triboelectric charge. This finding involves two different features: one is that even such a

Specimen	UV irradiation time (h)	Triboelectric[a] charge (kV)	Half decay[b] time (s)		% Decay[b] after 3 min	
			+5 kV	−5 kV	+5 kV	−5 kV
PS	0	−5.5	VL	VL	0.1	0.1
PS	1	−2.3	VL	VL	0.2	0.2
PS	2	−1.0	VL	VL	0.2	1.2
PS	5	−0.9	VL	VL	2.7	2.5
PET	0	−3.7	VL	VL	0.1	0.3
PET	1	−3.3	VL	VL	0.2	0.3
PET	2	−3.2	VL	VL	0.2	0.2
PET	5	−1.0	VL	VL	0.2	0.2
PET-g-DMAA	—	−0.5	18	21	78.0	80.0
PS-g-AA	—	−0.4	255	249	31.0	38.2

DMMA, N,N-dimethyl acrylamide; AA, acrylic acid.
[a] 25°C, 60% RH.
[b] 20°C, 75% RH. VL, very long (longer than 1 h).

hydrophilic polymer as PDMAA is inevitably charged to about 1 kV by rubbing when completely dried and stored below 60% RH, and the other is that it may be possible to prepare an antistatic material through surface grafting provided the material is to be used under an ambient condition at around 60% RH.

PET film was graft-polymerized with DMAA by the photoirradiation technique, as described elsewhere.[22] The triboelectric charge of surface-grafted PET film is given in Table I. The charge generated upon rubbing at 25°C and 60% RH is −0.5 kV and the half decay times, when +5 kV and −5 kV are initially applied, are as short as 18 and 21 s, respectively, in contrast to those of the UV-irradiated films. To determine the dependence of the electrostatic properties on the graft amount, the PET film was surface-grafted with acrylamide (AAm) since the amount of PAAm grafted was easily determined by the ninhydrin method.[18] As can be seen from the results shown in Figure 7, the decay time is reduced considerably with an increasing amount of PAAm grafted. Unless water is present, neither hydrophilic polymers such as PDMAA nor surface-grafted polymers with hydrophilic monomers become conductive at all, contrary to the electroconductive polymers and the polymers blended with metals or carbon. However, the surface having a large amount of water-soluble graft chains will absorb plenty of water when the surface is exposed to an environment of high humidity. The more hydrated surfaces will show lower decay times because the electric charge carriers may migrate more easily through the surface layer and be discharged more rapidly, as the surface is more hydrated.

If the graft chain possesses cationic or anionic groups, the surface-grafted material is expected to become more effective in antistatic property. Results of triboelectrification and decay of charges are shown in Figure 8 for the PET fabrics that were surface-grafted with various water-soluble monomers. The monomers employed for the surface graft polymerization onto the PET fabrics include sodium styrenesulfonate and 2-acrylamido-2-methylpropane sulfonic acid as anionic monomers and N,N-dimethylaminoethyl acrylate as cationic
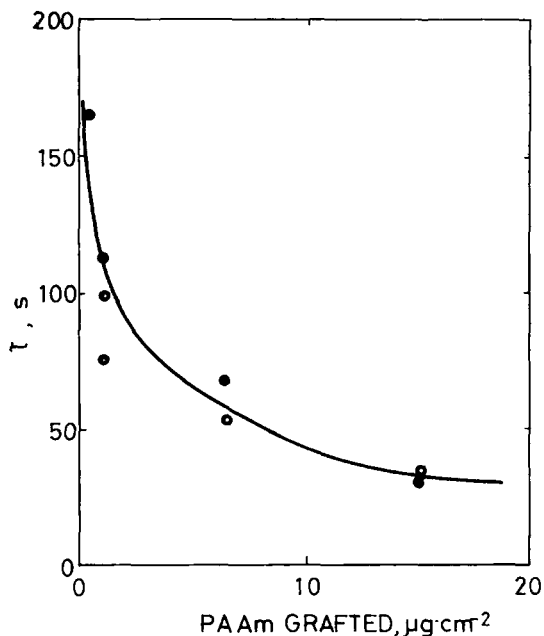
Fig. 7. Half decay time (τ) of grafted poly(ethylene terephthalate) films as a function of the amount of grafted polyacrylamide. The grafted films were initially exposed to electric fields of (○) +5 kV and (●) −5 kV.
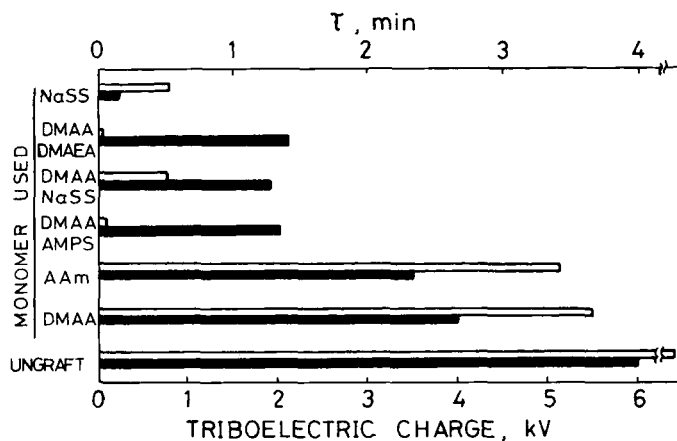

Fig. 8. Electrostatic properties of the poly(ethylene terephthalate) fabrics surface-grafted with various monomers. Triboelectric charge generated upon rubbing with a cotton fabric is given in absolute values neglecting the sign of the charge. Half decay time (τ) is the average of values observed when +5 kV and −5 kV were applied. Nass, sodium styrenesulfonate; DMAEA, *N,N*-dimethylaminoethyl acrylate; AMPS, 2-acrylamido-2-methylpropane sulfonic acid; □, half decay time; ■, triboelectric charge.

monomer in addition to nonionic monomers (DMAA and AAm). When graft polymerization of a single monomer was difficult, equimolar mixtures of two different monomers were used for graft polymerization. The half decay time of the ungrafted PET fabrics was around 1.5 h. Figure 8 indicates that electrostatic charging is more inhibited by graft polymerization of ionic monomers than of nonionic ones. However, one cannot give an answer to the question of which monomer, anionic or cationic, is more appropriate for reducing electrostatic charging. A more detailed study is currently underway to get a deeper insight into the triboelectrification of surface-grafted films and fabrics.

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