

# A Consideration of Secondary Electron Emission from Organic Solids

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## Synopsis

The behavior of the secondary electron emission (SEE) from organic solids has been considered. It has been shown that the maximum SEE yields of many hydrocarbon compounds exponentially depend on the extinction coefficient of secondary electron defined by the  $\pi$ -electron fraction in molecule, which is correlated to Dionne's theoretical equation. The concept that the extinction coefficient of secondary electron is represented in terms of the fraction of the delocalized and low energy-gap electron-like  $\pi$ -electron will be convenient for a rough estimation of the SEE yield of other various materials. On the other hand, a novel universal equation representing the normalized SEE yield curve has also been proposed in this paper, by which an analysis of the normalized SEE yield curves of many organic solids have been tried.

## INTRODUCTION

Organic solids are molecular aggregates which have weak intermolecular force. In such molecular compounds, their electron emission properties are directly related to the electronic structure of the molecule. That is, the electron emission characteristics greatly reflect the electronic property in the molecule, and the influence of the state of aggregation such as crystallinity and morphology is comparatively small. Such electron emission behavior is also different from nature, like the conduction behavior, depending on the long-distance order structure of conducting segments in the aggregates. The study of the electron emission from organic solids is an interesting research subject for relating their electronic property directly to the molecular structure. Photoelectric emission from organic solids has actively been studied with a view to analyzing electronic structures of organic molecules, which has given much information for the electronic property of organic molecules, e.g., the electron energy level, the ionization potential, etc.<sup>1</sup> On the other hand, the detailed study of secondary electron emission (SEE) from organic solids is comparatively rare. The authors have considered the trend of the SEE characteristics of various organic compounds in a previous paper,<sup>2</sup> which reported that the maximum SEE yield is higher for the aliphatic compound than for the aromatic and is higher for the organic solid with high ionization potential in analogy with the relationship between work function and maximum SEE yield for metals. Moreover, the authors have also reported that the SEE yield of the electron-conductive polymer composite of the conductive

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particles dispersed in a matrix polymer mainly depends on the SEE yield of the matrix polymer and is almost independent of the addition of the conductive particles having low SEE yields, probably due to the polymer-rich surface layer.

On the other hand, the relationship between the SEE yield and the molecular structure was considered early a few times in terms of the percentage content of carbon atom in organic solids by Matskevich and Mikhailova<sup>3</sup> and in terms of the  $N_e/N_{CH}$  ratio ( $N_e$  = the number of total electrons and  $N_{CH}$  = the number of C—H bonds in the molecule) by Bubnov and Frankevich.<sup>4</sup> However, these considerations have not explained the relationship very favorably. Burke<sup>5</sup> has recently analyzed the SEE yield data of polymers, independent of us, in terms of applying the valence electron density related to the mean free path of electron in organic solids derived by Ashley and Williams.<sup>6</sup> It has been reported in his paper that the SEE yield  $\delta$  is represented in terms of  $\delta = KE_p^{-n}$  ( $K$  = the emission coefficient and  $E_p$  = the primary electron energy) and can be understood by relating the value of  $K$  to the valence electron density.<sup>5,7</sup> In Burke's analysis, the SEE from polymers was, roughly, discussed. On the other hand, a theoretical analysis of SEE yield curves has been carried out by Dionne,<sup>8</sup> and it has been confirmed that Dionne's equation is in good agreement with many SEE data of inorganic solids for the locations of the crossover points on the yield curve.<sup>9</sup> This Dionne equation has also been applied in Burke's analysis mentioned above.

All organic solids consist of various molecular structures constructed on a carbon chain skeleton. In many of the organic solids the intercarbon bonds consist of two types of chemical bonds, i.e.,  $\sigma$ -bond and  $\pi$ -bond, which show quite different properties even in hydrocarbon compounds which have simple molecular structures. Even in the case of organic solids having the same valence electron number per molecular unit, their electronic properties are quite as different from each other as graphite and diamond. Therefore, it is more preferable to treat the valence electron density in which is taken into consideration the form of the electron orbitals. From this point of view, the authors considered the treatment due to the numbers of  $\pi$ -electron and  $\sigma$ -bond instead of the valence electron density, and studied on the relationship between the data of maximum SEE yields of organic solids and the numbers of  $\pi$ -electrons and  $\sigma$ -bonds. Moreover, the maximum SEE yields of organic solids take place at fairly low values of  $E_{pm} = 200\text{--}300$  eV, and the decreases in  $\delta$  are apparently large in the region of  $E_p > E_{pm}$  as compared with the inorganic solids. However, the normalized yield curves of organic solids do not show a large difference with the inorganic ones. Considering the better agreement with the experimental data, we have set up a novel universal equation representing the normalized SEE yield curve from a statistical consideration. By the equation, we have tried to analyze the normalized SEE yield curves of many organic solids which we measured.

## EXPERIMENTAL

The SEE yields were measured for the following materials: organic semiconductors (T, LT, KT, and NT shown in Table IV), polymers (PU, PI, XY, N4, N6, and N12 shown in Table IV), and polymer composites. T is 7,7,8,8-tetra-

TABLE I  
The Compositions of Polymer Composites

| Abbreviation | Material          | Composition (parts) |    |        |        |     |     |
|--------------|-------------------|---------------------|----|--------|--------|-----|-----|
|              |                   | PVC                 | PU | NaTCNQ | Carbon | ST1 | ST2 |
| CM           | PVC + PU          | 50                  | 30 | 0      | 0      | 0   | 0   |
| CN           | PVC + PU + NaTCNQ | 27                  | 30 | 40     | 0      | 1.5 | 1.5 |
| CK           | PVC + PU + KTCNQ  | 27                  | 30 | 40     | 0      | 1.5 | 1.5 |
| C1           | PVC + PU + C(1)   | 50                  | 30 | 0      | 20     | 0   | 0   |
| C2           | PVC + PU + C(2)   | 48                  | 30 | 0      | 20     | 1   | 1   |
| C3           | PVC + PU + C(3)   | 45                  | 30 | 0      | 20     | 0   | 5   |
| C4           | PVC + PU + C(4)   | 45                  | 30 | 0      | 20     | 5   | 0   |

cyanquinodimethane (TCNQ), and LT, KT, and NT are Li, K, and Na salts of TCNQ, respectively. As a matrix polymer for the polymer composite, poly(vinyl chloride) (PVC) plasticized by polyurethane (PU) ("Ultramoll PU" Bayer Co., Ltd.) was selected, and its SEE yield was also measured. As conductive particles, sodium TCNQ salt (NaTCNQ) or carbon black (CB) was used. The electron-conductive polymer composites were composed of the conductive particles and stabilizers (tribasic lead sulfate (ST1) and/or barium cadmium laurylate (ST2)) dispersed in the PVC + PU matrix, which were made by blending with heated rollers and were formed into a sheet of 1.5 mm thickness. The compositions of these composites are shown in Table I. The test samples for measuring the SEE yields were prepared as follows: crystal powders of organic semiconductors were molded into tablets of 1.5 mm thick and 1 cm in diameter under high pressure, and the polymers with high resistivity were formed into films of a few microns thick on aluminum plates. Each sample was cut into a disk 1 cm in diameter and was mounted on a target in the SEE measuring apparatus shown in a previous paper.<sup>2</sup> The SEE yield was measured by the dc method for organic semiconductors, and by the pulse beam method for the polymers and composites in order to avoid charge buildup on the sample surface. The incident electron beam current used was less than  $10^{-9}$  A, and its pulse width was 1 ms. The measurement was carried out under high vacuum less than  $10^{-8}$  torr in order to be free from contamination on the sample surface. The SEE yield  $\delta$  was determined from the equation  $\delta = I_c / (I_c - I_t)$ , where  $I_c$  and  $I_t$  are the collector current and the target current, respectively. In this measurement, the SEE yield  $\delta$  include the contribution of backscattered electrons and elastic scattered electrons.

## RESULTS AND DISCUSSION

### Relationship between Maximum SEE Yields and Molecular Structures

Many of organic solids consist of two types of  $\sigma$ -bond and  $\pi$ -bond, which show different properties. The  $\sigma$ -electron is a localized bonding electron between two bonding atoms. The  $\pi$ -electrons form a delocalized electron orbital among conjugated double bonds in molecule, which is often called the  $\pi$ -electron cloud. This delocalized  $\pi$ -electron system has a lower energy gap

than the  $\sigma$ -electron system and deactivates excited electrons such as the secondary electron produced in the organic solids. Such difference of characteristics between  $\sigma$ -electron and  $\pi$ -electron is similar to that between diamond and graphite. From such a point of view, an assumption that an absorption constant of secondary electrons in organic solid is related to the  $\pi$ -electron density, i.e.,  $\pi$ -electron fraction per molecular unit, will be reasonable. Here, we define the  $\pi$ -electron fraction  $f_\pi$  as  $f_\pi = \pi_e/(\pi_e + \sigma_b)$ , where  $\pi_e$  is the number of  $\pi$ -electrons per molecule or monomer unit and  $\sigma_b$  is the number of  $\sigma$ -bonds existing outside the  $\pi$ -electron clouds. In the case of benzene, for example, the values are  $\pi_e = 6$ ,  $\sigma_b = 6$ , and  $f_\pi = 1/2$ . The  $f_\pi = 1/2$  for benzene is also nearly coincident with its geometrical fraction of  $\pi$ -electron per molecular unit, preferably. In such a consideration, core electrons in molecule and  $\sigma$ -bonds inside the  $\pi$ -electron cloud, even though the valence bond electron, are neglected. Since in the segment surrounded by the  $\pi$ -electron cloud the  $\pi$ -electron system absorbs and deactivates the excited high-energy electrons, the  $\pi$ -electron fraction can be treated as the absorption constant of excited electrons. Moreover, it is convenient for the estimation of SEE yield that the absorption constant of secondary electron can be easily estimated from the molecular structure of materials.

The SEE yield  $\delta$  is theoretically represented as the following equation by Dionne<sup>8</sup>:

$$\delta = (B/\zeta)(An/\alpha)^{1/n}(\alpha d)^{1/n-1}[1 - \exp(-\alpha d)] \quad (1)$$

where  $B$  is the escape probability,  $\zeta$  is the secondary electron excitation energy,  $\alpha$  is the secondary electron absorption constant,  $A$  is the primary electron absorption constant,  $d$  is the maximum penetration depth, and  $n$  is the power-law exponent.  $d$  is represented as  $d = E_p^n/An$  ( $E_p$  = the primary electron energy). From the analysis of  $\partial\delta/\partial(\alpha d) = 0$  of eq. (1), Dionne<sup>8</sup> has also shown the following equation for giving the maximum SEE yield  $\delta_m$ :

$$\alpha d_m = (1 - 1/n)[\exp(\alpha d_m) - 1] \quad (2)$$

where  $d_m$  is the value of  $d$  giving  $\delta_m$  and is equal to  $E_{pm}^n/An$  ( $E_{pm}$  = the value of  $E_p$  giving  $\delta_m$ ). From eq. (1), the maximum SEE yield  $\delta_m$  is

$$\delta_m = (B/\zeta)(An/\alpha)^{1/n}(\alpha d_m)^{1/n-1}[1 - \exp(-\alpha d_m)] \quad (3)$$

From eqs. (2) and (3), the following equation is derived:

$$\delta_m = (B/\zeta)[E_{pm}/(1 - 1/n)]\exp(-\alpha d_m) \quad (4)$$

Equation (4) corresponds to the function form which represents the absorption of secondary electrons in the diffusion process to surface. This equation is similar to the formulas for the light absorption of Lambert-Beer law and the light scattering.

Here, when considering the value of  $\delta_m$  for various materials, in analogy with the above-mentioned light absorption law, the absorption term  $\exp(-\alpha d_m)$  should be represented as  $\exp(-\alpha' d_m \rho)$ , where  $\alpha'$  is the extinction

TABLE II  
Maximum SEE Yields and  $\pi$ -Electron Fractions of Various Hydrocarbons

| Abbreviation | Material     | $\pi_e$ | $\sigma_b$ | $f_\pi$ | $\delta_m$ | $\ln \delta_m$ | Ref. |
|--------------|--------------|---------|------------|---------|------------|----------------|------|
| BE           | Benzene      | 6       | 6          | 0.500   | 1.66       | 0.507          | 10   |
| NA           | Naphthalene  | 10      | 8          | 0.556   | 1.52       | 0.419          | 10   |
| AN           | Anthracene   | 14      | 10         | 0.583   | 1.38       | 0.322          | 10   |
| PH           | Phenanthrene | 14      | 10         | 0.583   | 1.55       | 0.438          | 10   |
| TH           | Tetracene    | 18      | 12         | 0.600   | 1.46       | 0.378          | 11   |
| PY           | Pyrene       | 16      | 10         | 0.615   | 1.50       | 0.405          | 11   |
| DI           | Diphenyl     | 12      | 11         | 0.522   | 1.70       | 0.531          | 10   |
| GC           | Graphite     | 6       | 0          | 1       | 1.00       | 0              | 3    |
| DC           | Diamond      | 0       | 4          | 0       | 2.80       | 1.030          | 12   |
| PE           | Polyethylene | 0       | 6          | 0       | 2.85       | 1.047          | 3    |
| PS           | Polystyrene  | 6       | 11         | 0.353   | 2.10       | 0.742          | 3    |

coefficient and  $\rho$  is the factor depending on the electron density of material. Using the  $\pi$ -electron fraction  $f_\pi$  mentioned above, we define the extinction coefficient of secondary electron  $\alpha'$  as follows;

$$\alpha' = Cf_\pi + D \quad (5)$$

where  $C$  and  $D$  are the proportional constants ( $C > 0$  and  $D > 0$ ).

Here, we try to compare with the experimental data. The SEE yield data and  $\pi$ -electron fraction of various hydrocarbon compounds are tabulated as Table II, and are graphically shown in Figure 1. The  $\ln \delta_m - f_\pi$  relation shows a straight line in the figure, and the following equation is determined:

$$\ln \delta_m = -1.08f_\pi + 1.08 \quad (6)$$

$$\delta_m = 2.95 \exp(-1.08f_\pi) \quad (7)$$

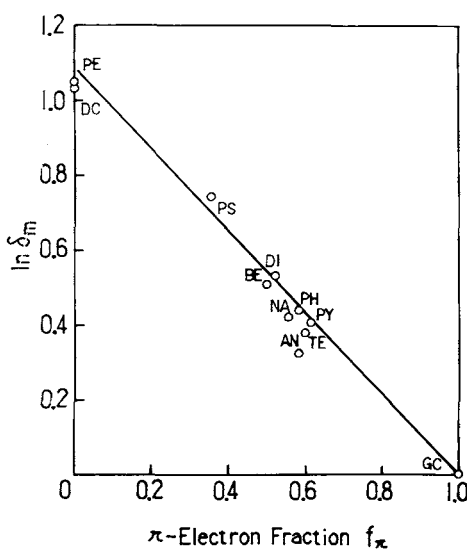


Fig. 1. Relationship between maximum SEE yield and  $\pi$ -electron fraction for hydrocarbons.

From the relation among eqs. (4), (5), and (7), the following semiempirical equation applicable to all hydrocarbon compounds will be suggested:

$$\delta_m = \delta_0 \exp(-Cf_\pi d_m \rho) \quad (8)$$

The relationship between eqs. (7) and (8), as a result, suggests that the values of  $d_m \rho$  will be approximately equal in all hydrocarbons. However, the confirmation by experimental data has not been performed yet because of the unknown values of  $d_m$ . Moreover, if describing in detail, for example, all of hydrocarbons with no  $\pi$ -electron must show  $\delta_m = 2.95$  by eq. (7) irrespective of their molecular structures similarly from diamond to polyethylene. Such a treatment in this paper is a method for a rough estimation of the maximum yield, and detailed analyses for SEE yields of these organic solids should be performed on the basis of many exact SEE yield data hereafter. Physical analyses for SEE phenomena studied heretofore, even for inorganic solids, are markedly complicated.<sup>13</sup> The above-described eq. (8) represents a universal relationship between the maximum SEE yield and the molecular structure in all organic solids including no heteroatoms. Since the  $\pi$ -electron fraction is the value which can be geometrically determined from the molecular structure, such a treatment is not based on the concept of solid state physics. However, by means of such a simple treatment based on molecular structure, we have gotten an agreeable result as described above.

This consideration needs to be extended so as to be applicable to all organic solids. However, organic solids containing heteroatoms such as N, O, S, halogen, and metal atoms have been composed of diverse electron orbitals, and the simple treatment as above would be difficult. However, from such a point of view, the semiempirical equation which is applicable to all organic solids, may be derived by means of adding compensation factors for heteroatoms such as a parameter of the Coulomb integral for heteroatom in the molecular orbital theory.<sup>14</sup> In general, electronic states in organic solids are often treated with molecular orbital theory composed of combining atomic or valence bond orbitals, by which electronic states such as ionization potential, electron affinity, etc., have been determined. However, different from the incidence of photon, the incidence of the charged particle such as electron to an organic solid generally excites a part of electrons in molecule, but ionizes the many other parts of electrons and produces secondary electrons. The generated secondary electrons in solid consecutively cause the ionization in larger cross section. Therefore, the SEE behavior will be affected not only by one energy level of electron such as ionization potential, but also considerably by the fraction of each electron energy level, i.e., the geometrical distribution of energy levels. Therefore, such a simple method for estimating the absorption constant of secondary electron from the molecular structure is practically convenient and the extended treatment which is applicable to many organic solids containing heteroatoms will be significant. We have already tabulated many data of the maximum SEE yields of organic solids containing heteroatoms together with our measured data, in the previous paper.<sup>2</sup> The later known SEE data of various organic compounds are shown in Table III. In this table, the SEE yield data from organic liquids has also been shown, for which Doblhofer et al.<sup>15</sup> have reported that the liquid polymer shows a different

TABLE III  
The Maximum SEE Yields of Various Organic Compounds

| Material                     | Chemical structure                    | $\delta_m$ | $E_{pm}$<br>(eV) | Ref.            |
|------------------------------|---------------------------------------|------------|------------------|-----------------|
| Solid                        |                                       |            |                  |                 |
| Nylon 4                      | $(C_3H_6NHCO)_n$                      | 2.39       | 230              | EX <sup>a</sup> |
| Nylon 6                      | $(C_5H_{10}NHCO)_n$                   | 2.53       | 240              | EX <sup>a</sup> |
| Nylon 12                     | $(C_{11}H_{22}NHCO)_n$                | 2.60       | 240              | EX <sup>a</sup> |
| Polyvinylide<br>fluoride     | $(CH_2CF_2)_n$                        | 2.5        | 250              | 7               |
| Metal-free<br>phthalocyanine | $C_{32}H_{18}N_8$                     | 1.33       | 200              | 4               |
| Copper<br>phthalocyanine     | $C_{32}H_{16}CuN_8$                   | 1.38       | 250              | 4               |
| Liquid                       |                                       |            |                  |                 |
| Poly(ethylene<br>glycol)     | $(CH_2CH_2O)_n$                       | 2.7        | 250              | 15              |
| Diocetyl sebacate            | $C_8H_{17}OCO(C_8H_{16})COOC_8H_{17}$ | 2.8        | 200              | 16              |
| Glycerin                     | $CH_2(OH)CH(OH)CH_2(OH)$              | 2.6        | 200              | 17              |

<sup>a</sup>EX = data measured by the authors.

SEE behavior as compared with the chemically similar solid polymer films. The analysis of these data in Table III is needed in the future. Moreover, if the SEE behavior can be related to, for example, the electronic polarization, the electron spin concentration, etc., it will be further significant.

This concept that the delocalized electron orbital greatly contributes to the absorption constant of secondary electron, and that the valence and core electrons in the inside of the delocalized electrons are negligible, may be also effective in analyzing the SEE yields of inorganic solids. When adding the contribution of such a delocalized electron fraction to the conventional factors such as the ionization potential, the valence electron, and the atomic number,<sup>13</sup> the SEE yields may be more correctly estimated from the molecular structure.

In general, in polymeric materials the ionization by radiant ray is easily caused and the polymeric materials are subject to decomposition as compared with inorganic solids. As chemical reaction by radiation, there are two types of reactions, degradation and crosslinking, and the chemical structure irreversibly changes. However, the polymeric materials have the protective effect such as the "sponge" and the "cage" effects against radiant rays.<sup>18</sup> The "sponge" effect is the protection that the excited electrons by radiation are deactivated through the delocalized  $\pi$ -electron orbital in polymeric molecules, and the "cage" effect is the effect that the molecular segment having a dissociated radical recombines during capture by the tangle of long polymer chains. Therefore, aromatic polymers with the delocalized  $\pi$ -electrons show higher radiant durability than aliphatic polymers with the localized  $\sigma$ -electrons. Thus, although apparently a considerable amount of energy is dissipated in the ionization and the electron displacements, the many generated ion radicals recombine and convert the ionization energy into heat without producing any chemical change. Therefore, although the energy of chemical bond is a few eV, actual energy which causes a chemical change by radiation is

as high as 30–35 eV. Such a radiation durability is also represented by the  $G$  value, which is defined as the number of chemical changes per absorbed energy of 100 eV. The  $G$  value indicates that  $G < 0.1$  is stable,  $G > 10$  is sensitive, and  $G > 100$  is a chain reaction, against radiation. The  $G$  values of some organic polymers are, for example, 2.0 (polyethylene), 0.3 (polyamide), 0.2–0.5 [poly(vinyl chloride)], and 0.04–0.06 (polystyrene),<sup>19</sup> where the very low  $G$  value of polystyrene indicates stabilization effect of delocalized  $\pi$ -electrons against radiation.<sup>18</sup> Such a radiation durability is due to the interaction between the bonding electrons and the excited electrons produced by radiation. Therefore, it is considered that the SEE behavior also has a partially similar process and the secondary electrons produced in solid are stabilized in a similar manner. That is, the above-mentioned analysis that the extinction coefficient of secondary electron is defined in terms of the  $\pi$ -electron fraction is not also in conflict with such a tendency of the radiation durability.

### A Consideration of Normalized SEE Yield Curves of Organic Solids

A theoretical analysis of SEE yield curves has been carried out by Dionne,<sup>8</sup> and it has been confirmed that Dionne's equation is in good agreement with many SEE yield data.<sup>5,9,20</sup> However, the agreement is comparatively rough and is not necessarily good-coincident in the region from  $E_{pm}$  to a few keV. Our measured SEE yield data were also similar to that; that is, the  $\ln(\delta/\delta_m) - \ln(E_p/E_{pm})$  plots of these data were not always linear even in the high  $E_p/E_{pm}$  region. From the form of the  $\delta/\delta_m - E_p/E_{pm}$  curves, we felt that the dependence of  $\delta/\delta_m$  on  $\log(E_p/E_{pm})$  may show a Gaussian distribution, and quite empirically set up an universal equation which can allow better to agree with the normalized SEE yield curves of the organic solids in the region from  $E_{pm}$  to 1.4 keV, which is the maximum  $E_p$  in our measurement.

The SEE phenomenon is generally electron emission from solid caused by the Coulomb repulsion against incident high-energy electrons (electron–electron interaction) in which the surrounding electrons at various energy levels are excited and the molecules are ionized. These excited electrons further excite the other surrounding electrons and are deactivated themselves till reaching the gap energy. In such a scattering process of secondary electron in organic solids, the delocalized  $\pi$ -electron system greatly contributes to the deactivation of the secondary electrons in solid. These secondary electrons diffuse, and some of them are emitted from a surface. Therefore, it is considered that the SEE yield, different from the photoelectric emission, will be statistical characteristics caused by the electron–electron interaction in various energy levels. It is therefore plausible to consider that the SEE yield will obey the statistical distribution functions. From such a point of view, we treat our measured SEE yield data by the following universal equation:

$$\delta/\delta_m = 1/\left\{\beta \left[|\ln(E_p/E_{pm})|\right]^s + 1\right\} \quad (9)$$

where  $\beta$  is the material constant and  $s$  is the constant near 2.0.

Equation (9) is a universal function form which has been set up on the basis of  $\log(E_p/E_{pm})$ . As a few typical curves among our measured  $\delta - E_p$  character-



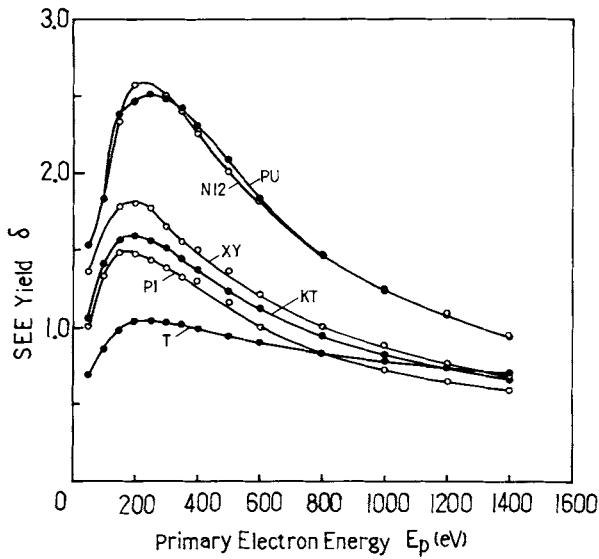


Fig. 2. SEE yield curves of TCNQ, KTCNQ, polyimide, xylene resin, polyurethane, and nylon 12.

istics of organic solids, the  $\delta-E_p$  curves for TCNQ (T), KTCNQ (KT), polyimide (PI), xylene resin (XY), polyurethane (PU), and nylon 12 (N12) are shown in Figure 2. When analyzing, for example, the  $\delta-E_p$  data in the  $E_p > E_{pm}$  region for TCNQ and nylon 12 by eq. (9), their data are plotted as shown in Figure 3, and show straight lines, respectively. All data in the  $E_p > E_{pm}$  region for the other organic solids similarly showed straight lines.

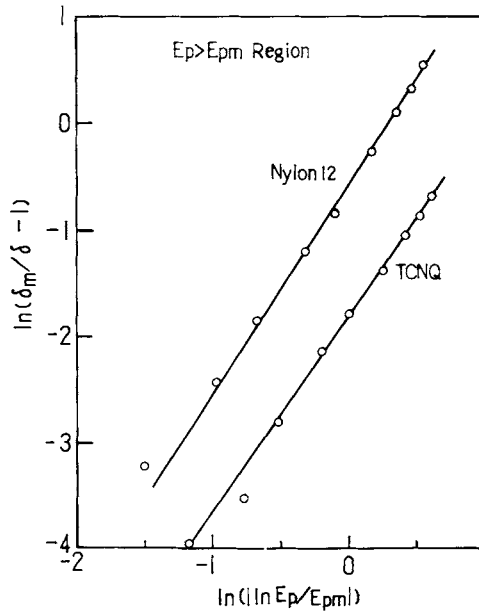


Fig. 3. SEE yield plots of TCNQ and nylon 12 in the  $E_p > E_{pm}$  region.

TABLE IV  
The Values of  $s$  and  $\beta$  Determined from Eq. (9)

| Abbreviation | Material          | $\delta_m$ | $E_{pm}$<br>(eV) | $E_p < E_{pm}$ region <sup>a</sup> |         | $E_p > E_{pm}$ region |         |
|--------------|-------------------|------------|------------------|------------------------------------|---------|-----------------------|---------|
|              |                   |            |                  | $s$                                | $\beta$ | $s$                   | $\beta$ |
| T            | TCNQ              | 1.05       | 220              | 1.48                               | 0.300   | 1.85                  | 0.162   |
| LT           | LiTCNQ            | 1.34       | 190              | 1.71                               | 0.268   | 2.00                  | 0.324   |
| KT           | KTCNQ             | 1.59       | 200              | 2.18                               | 0.289   | 2.08                  | 0.352   |
| NT           | NaTCNQ            | 1.60       | 200              | (1.71)                             | (0.268) | 2.16                  | 0.326   |
| PU           | Polyurethane      | 2.51       | 260              | (2.18)                             | (0.289) | 2.15                  | 0.538   |
| PI           | Polyimide         | 1.49       | 180              | (2.04)                             | (0.309) | 2.18                  | 0.325   |
| XY           | Xylene Resin      | 1.80       | 200              | (2.09)                             | (0.160) | 2.08                  | 0.403   |
| N4           | Nylon 4           | 2.39       | 230              | 1.76                               | 0.288   | 2.10                  | 0.487   |
| N6           | Nylon 6           | 2.53       | 240              | (1.89)                             | (0.613) | 2.13                  | 0.509   |
| N12          | Nylon 12          | 2.60       | 240              | (1.93)                             | (0.507) | 1.96                  | 0.549   |
| CM           | PVC + PU          | 2.74       | 260              | 1.85                               | 0.458   | 1.87                  | 0.472   |
| CK           | PVC + PU + KTCNQ  | 2.72       | 250              | 2.11                               | 0.190   | 2.07                  | 0.368   |
| CN           | PVC + PU + NaTCNQ | 2.46       | 230              | (2.11)                             | (0.190) | 2.08                  | 0.352   |
| C1           | PVC + PU + C(1)   | 2.30       | 275              | 1.80                               | 0.198   | 1.98                  | 0.533   |
| C2           | PVC + PU + C(2)   | 2.41       | 290              | 1.66                               | 0.270   | 1.87                  | 0.546   |
| C3           | PVC + PU + C(3)   | 2.42       | 220              | (1.82)                             | (0.517) | 2.08                  | 0.350   |
| C4           | PVC + PU + C(4)   | 2.47       | 250              | 1.87                               | 0.487   | 2.08                  | 0.391   |

<sup>a</sup>( ) = unreliable value determined from poor linearity.

From them, the values of  $s$  and  $\beta$  were determined by applying eq. (9) (Table IV). In the region of  $E_p < E_{pm}$ , their linearities are not necessarily good, and the determined values of  $s$  and  $\beta$  are not reliable enough. One of the reasons is because of the poor accuracy of the SEE measurement in low  $E_p$  region. Another reason is that, in the  $E_p < E_{pm}$  region, the generation of secondary electron dominates the SEE yield in contrast to the  $E_p > E_{pm}$  region in which the diffusion of secondary electron to surface is predominant. In the region of  $E_p > E_{pm}$ , the determined values of  $s$  and  $\beta$  are reliable, and the values of  $s$ , as shown in Table IV, were determined to be within  $2.0 \pm 0.2$  for all measured materials. On the other hand, the values of  $\beta$  do not show constant values among various materials. The relationship between  $\delta_m$  and  $\beta$  is plotted in Figure 4. The  $\delta_m$ - $\beta$  relation is approximated by the equation  $\delta_m = 5.64\beta^2 + 0.9$ , and the  $\beta$  value is approximately represented as  $\beta = [(\delta_m - 0.9)/5.64]^{1/2}$  from the equation. The  $\log(\delta/\delta_m)$ - $\log(E_p/E_{pm})$  plots for nylon 12 (N12) and TCNQ (T) showing the maximum and minimum values of  $\beta$ , respectively, are shown in Figure 5, in which they have different slopes from each other. The  $\beta$  value will be probably the function of the  $\pi$ -electron fraction in the molecule as mentioned above, but, for such molecules including heteroatoms, their values of  $f_\pi$  are not clear.

In Figure 4, the plots of the composite materials, CM, CN, CK, C3, and C4, deviate from the tendency for the other single materials. This result will be understood from the following consideration. The surface of the composite materials is not always uniform because of the influence of the forming process and shows diverse composition. Near the surface of composite materials, the exudate layer such as a polymer-rich layer or an additives layer is generally formed due to the exudation effect in the forming process of sample,

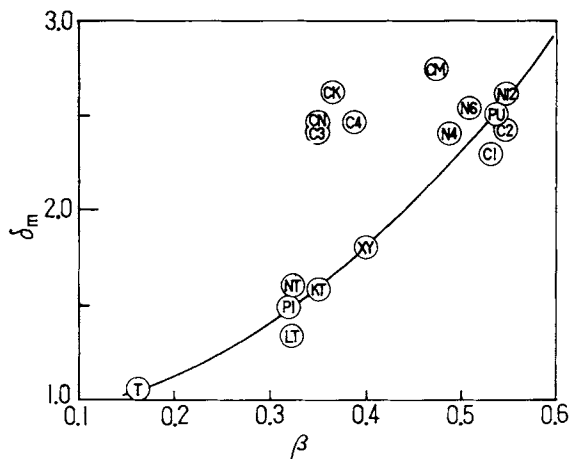


Fig. 4. Relationship between  $\delta_m$  and  $\beta$  in the  $E_p > E_{pm}$  region.

and hence the near-surface layer is composed of two layers as shown in Figure 6. Consequently, the  $\delta-E_p$  curve of the composite material will be represented as the complexing of each  $\delta-E_p$  curve of the two layers as shown in Figure 6. Since these composite materials are composed of the conductive particles of low SEE yield dispersed in a matrix polymer of high SEE yield, as a result, the  $\beta$  values of these composite materials show higher value than the above-mentioned tendency for the single material. The deviations of CM, CN, and CK will be mainly due to the exudation of PU, and those of C3 and C4 to the exudation of stabilizer, ST1 or ST2, with high SEE yields themselves. If extensively applying such a method to unknown composite material, the state of the surface layer and its thickness may be able to be analyzed in terms of the difference from the universal relationship between  $\delta_m$  and  $\beta$ .

As a result of a consideration of the SEE yields of hydrocarbon compounds, in conclusion, we have shown that the maximum SEE yield  $\delta_m$  is related to

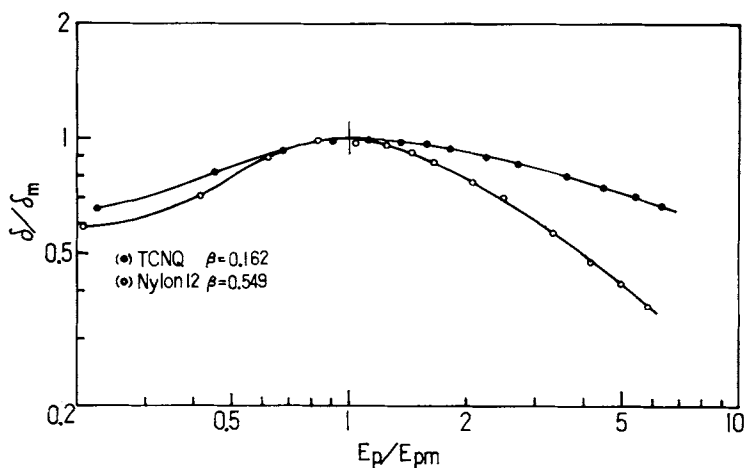


Fig. 5.  $\log(\delta/\delta_m)$ - $\log(E_p/E_{pm})$  plots of TCNQ and nylon 12.

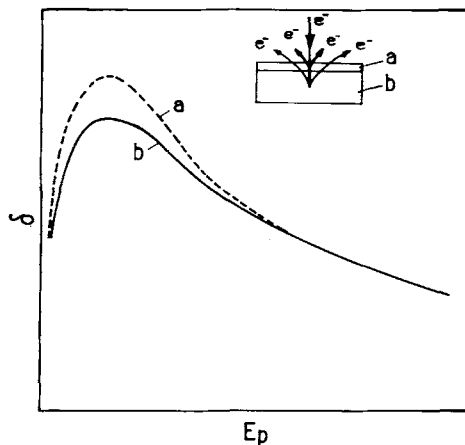


Fig. 6. Model of  $\delta$ - $E_p$  curve for polymer composite.

the extinction coefficient of the secondary electron defined by the  $\pi$ -electron fraction  $f_\pi$  and is represented in terms of  $\delta_m \propto \exp(f_\pi)$ . Moreover, we have also shown that the normalized yield curve is represented as the equation  $\delta/\delta_m = 1/\{\beta[|\ln(E_p/E_{pm})|^s + 1]\}$ , which is obtained from a statistical consideration, and we have correlated the value of  $\delta_m$  to the material constant  $\beta$ . The values of  $\delta_m$  for composites have been considered relating to the  $\delta_m$ - $\beta$  relation. We expect that this consideration will give a suggestion to the investigation on the SEE behavior of organic solids.

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