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SECONDARY EMISSION FROM POLYMERS

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The available data on secondary emission yields from electron bombarded polymers was reviewed to identify those features they have in common with metals and inorganic insulators. As in the case of the more widely studied materials it was found that when the yield δ obtained at a bombarding electron energy E_0 , is divided by the maximum yield δ_m , and plotted versus E_0/E_{om} , most of the data falls within a small range, i.e. on a "universal" curve. At high energies the yield is given by a simple power function $\delta = KE^{-n}$ with $n = 0.725$ for all the materials and K ranging from 1.55 for teflon to 0.68 for kapton if E is in KeV. The value of K is found to decrease as the complexity of the repeating unit in the polymer increases. This can be expressed quantitatively as $K = 10.64 (N/M) - 3.15$ where N/M is the ratio of the number of valence electrons to the gram molecular weight of a monomeric unit. We also find that δ_m/E_{om} averages 9.5 for the polymers which is very close to the value of 9.6 reported for inorganic insulators. Using the semiempirical model of secondary emission we find that the yield coefficient is given by $K = 12.1E_{om}^{1.725}$. Consequently it is possible to estimate the yield curve over the full range of interest if any one of the parameters δ_m , E_{om} or K are known. Data is given for polyethylene, polyvinylalcohol, polamide, lucite, polystyrene, mylar, teflon, kapton, and two halogenated forms of styrene.

Introduction

Data on secondary electron emission yields from electron bombarded polymers is required for modeling charge build-up on spacecraft. Information in the literature has been limited with respect to both the range of bombarding energies and materials studied. Here we show that secondary emission from polymers can be described using theoretical models developed for other classes of materials¹. Sufficient data is provided to reproduce emission results on eight common polymers. When supplemented with empirical results, it appears possible to extend the reported findings to bombarding energies and materials for which information is unavailable.

It is customary to distinguish between two components of the emission from electron bombarded materials: "true" secondary electrons (energy less than 50 eV), and backscattered primaries. The usual notation is δ for secondaries, η for backscattered primaries and σ for the total emission (all based upon emission per incident primary electron). These quantities are related at any given bombarding energy by the expression

$$\sigma = \delta + \eta \quad (1)$$

δ and η exhibit a different dependence upon the incident electron energy and therefore, are best treated separately. The maximum value of δ and the energy at which it occurs is indicated by δ_m and E_{om} respectively.

In this paper we first briefly review the available data on secondary emission yields from polymers. We then examine this information to see whether or not certain characteristics found for metals and inorganic insulators can be identified. These characteristics

include: the ability to construct a universal yield curve if δ_m and E_{om} are known, a power function dependence of the yield on electron bombarding energy at high energies, and a simple constant relation between δ_m and E_{om} . We then examine the semiempirical model developed for other materials in order to identify relationships between observable parameters that would permit maximum application of the limited existing data.

Experimental Studies of Secondary Emission From Polymers

Very few experimental studies of secondary emission from polymers have been reported to date²⁻⁵. In the work by Matskevich² the total yield σ was determined for eight different polymers over the 0.2 to 2.4 keV range of electron bombarding energies. The backscatter coefficient η was also measured for the same polymers thereby permitting a determination of the secondary emission yield δ by using Eq. (1). Both σ and η were determined for an angle of incidence of 60° as well as 0°. The maximum yields σ_m and δ_m and the bombarding energy E_{om} at which they occur are given in Table 1.

In the study by Kazantsev and Matskevich³ the total yield σ and backscatter coefficient η were measured for polymethyl methacrylate at bombarding energies between 3 to 25 keV and for incident angles between 0 to 60°.

Willis and Skinner⁴ measured the total yield σ over the 0.05 to 2.5 keV energy range for four different types of polymers. Studies included two commercial forms of one of the polymers for a total of five different materials. The dependence of yield on the angle of incidence and measurements of backscatter were not included.

Gair⁵ reported measurements on three different polymers for bombarding electron energies in the 8-80 keV range and at 0°, 30°, 45° and 60° incident angles.

Analysis of the Data

As is the case with metals, the polymers show a maximum in the number of secondary electrons emitted per incident primary (δ_m), at a bombarding energy (E_{om}), characteristic of the given material. For metals it has been shown that if the ratio of the yield at any energy to the maximum yield (reduced yield δ/δ_m) is plotted versus the reduced energy (E_0/E_{om}), the experimental observations fall on a universal curve.

Willis and Skinner⁴ found that when they plotted σ/σ_m versus E_0/E_{om} , their data points, with the exception of Teflon, fell within a narrow region resembling reduced yield curves previously reported for metals. The shape was somewhat different than that for metals, falling off more rapidly at large values of E_0/E_{om} . We find that the data of Matskevich² also results in a universal curve as shown in Fig. 1. We will compare the two results after discussing how such a curve can be derived from the semiempirical theory of secondary emission described by Dekker¹.

For metals at bombarding energies several times greater than that at which the maximum yield occurs, emission has been found to be proportional to the electron collision stopping power⁶⁻⁸. Over a limited energy range, such as that considered here (0.5 to

100 keV), the stopping power can be represented by a simple power function. In addition, according to Makhov⁹ the secondary electron yield for eighteen different materials shows a simple power dependence on bombarding electron energy. We will show that the semiempirical model of secondary emission also predicts a power function dependence on energy. All of the available data was examined to determine if this behavior extended to the polymers. This proved to be the case for the data examined all of which can be described by the expression

$$\delta = kE_0^{-n} \quad (2)$$

Henceforth we will express E_0 in units of keV. Values of n between 0.70 and 0.75 provided a satisfactory fit in most cases. A value of $n = 0.725$ was selected. Stopping powers for polymers in the 1 to 10 keV range¹⁰ and at 10 to 100 keV¹¹ fit a power function with similar values of n .

The low energy data of Matskevich for polyethylene and polymethyl methacrylate matches the high energy data of Gair and Kazantsev very well as shown in Fig. 2. We found that all of the Matskevich, Gair and Kazantsev results could be described using the same value of n in Eq. (2). This value of $n = 0.725$ also provided a satisfactory fit to the electron stopping powers of the polymers.

The agreement of the Gair results with the data of Willis and Skinner for Mylar and Kapton is not so good as can be seen in Fig. 3. The Kapton results represent the greatest departure from the rest of the polymer data. The failure of the Willis and Skinner data to agree with that of other authors, and in particular, the fact that it does not show the same energy dependence as the electron stopping power, places it far outside of the general pattern observed in all other secondary emission studies. Consequently, we will focus upon the other data sources^{2,3,5} which agree with one another and show internal consistency.

Values of the coefficient K in Eq. (1) are given in Table II based on the data of Matskevich, Kazantsev, and Gair. K is directly proportional to the emission efficiency of a given polymer. Examination of the tabulated values reveals a clearly discernable pattern. The value of K appears to be directly related to the complexity of the repeating unit in the polymer. In general the magnitude of K takes on its largest value for the simplest polymers $(CH_2)_n$ and $(CF_2)_n$ and is a minimum for the most complex $(C_{22}H_{10}N_2O_5)_n$, which is Kapton. In the process of attempting to express this relationship quantitatively we noted that Ashley^{10,12} had found that the electron stopping power for many polymers was a simple function of the ratio of the valence electrons (N) in a monomeric unit to its gram molecular weight (M). This holds for polymers containing just hydrogen, carbon, nitrogen, and oxygen with associated valence electrons taken as 1, 4, 5, and 6 respectively. We found that the K values in Table II plotted versus N/M follow a linear relationship as shown in Fig. 4. A least squares fit gives the expression

$$K = 10.64(N/M) - 3.15 \quad (3)$$

This means that with our knowledge of n , and K determined from Eq. (3) we can predict high energy emission values for a large class of polymers. It would appear that polyethylene represents the most efficient emitter within this class and Kapton is about the least efficient that can be expected.

We next examine the relationship between δ_m and E_{om} . In the course of using an atomic model for

describing the penetration of low energy electrons in solids Kanaya and Kawakatsu¹³ found that experimental values of δ_m and E_{om} were simply related for different classes of materials. In particular they noted that for 70 different elements the ratio of δ_m/E_{om} averages ~ 2.6 (E_{om} in keV). Actually, the values gradually change from a high of 3.3 for beryllium to a low of 2.2 for thorium. In a later paper Kanaya et. al.¹⁴ calculated values of δ_m and E_{om} for twenty inorganic insulators. In this case the ratio of δ_m/E_{om} averages ~ 9.6 , a value distinctly different from that previously found for the elements. As can be seen from Table I, with the exception of Teflon, the Matskevich values for δ_m/E_{om} agree very closely. If Teflon is eliminated they average 9.5! This may indicate that a different relation for δ_m and E_{om} will be required for heavily halogenated polymers.

Application of the Semiempirical Model to Polymers

Since most of the existing polymer secondary emission yield data appears to follow a pattern previously observed for metals and inorganic insulators it is worth exploring the possible application of the semiempirical model developed for those materials. Our objective is to identify additional relationships between the experimentally observable quantities δ_m , E_{om} , K and n that could be employed to extrapolate the existing data to energy ranges that have yet to be studied.

In the "constant-loss" form of the semiempirical theory described by Dekker¹ it is assumed that the average rate of energy loss by the primary bombarding electrons is given by $E_0/R(E_0)$ where R is their range. It is further assumed that the electron range is given by a power law i.e.

$$R = E_0^{n+1}/A(n+1) \quad (4)$$

where A is a constant characteristic of the material. In addition the probability that a secondary electron created at a depth x will escape to the surface is taken as

$$p(x) = B \exp(-\alpha x) \quad (5)$$

where B is a constant close to unity and α determines the "absorption" of secondaries. If ϵ is the average energy required to produce a secondary electron inside the solid then the above assumptions lead to a value for the yield at a bombarding energy E_0 given by

$$\delta = (BE_0/\alpha\epsilon R) (1 - \exp(-\alpha R)) \quad (6)$$

Using Eq. (4)

$$\delta = (B/E)(A/\alpha) \frac{1}{n+1} (-1 \exp(-Z^{n+1}))/Z^n \quad (7)$$

$$\text{or } \delta = (B/E)(A/\alpha) \frac{1}{n+1} g_n(Z)$$

$$\text{where } Z = Z_m E_0 / E_{om} \quad (8)$$

$$\text{and } g_n(Z) = (1 - \exp(-Z^{n+1}))/Z^n \quad (9)$$

Z_m represents the value for which $g_n(Z)$ reaches its maximum value.

A universal yield curve can be derived from Eq. (7) in the form

$$\delta/\delta_m = g_n(Z_m E_0 / E_{om}) / g_n(Z_m) \quad (10)$$

It can be seen from Eq. (10) that at high energies δ is simply proportional to E_0^{-n} which is consistent with experimental observations, i.e.

$$\delta = \frac{Z_m^{-n} E_{om}^n \delta_m E_0^{-n}}{g_n(Z_m)} \quad (11)$$

Relating this to our empirical finding we see that

$$K = Z_m^{-n} E_{om}^n \delta_m / g_n(Z_m) \quad (12)$$

This gives us a second relation between δ_m and E_{om} . For $n = 0.725$, $Z_m^{-n}/g_n(Z_m)$ equals 1.273 therefore

$$K = 1.273 \delta_m E_{om}^n \quad (13)$$

$$\text{or } K = 12.09 E_{om}^{n+1}$$

Using Eq. (13) we can determine δ_m if we know the value of K and thereby deduce the entire yield curve! Dionne¹⁵ gives additional useful relationships derivable from the model. In particular the lower and upper cross over points where $\delta = 1.0$.

Making use of Eq. (10) we can plot universal yield curves for the data of Willis and Skinner and that of Matskevich. The former found that $n = 1.0$ best represented their data. In that case $Z_m = 1.121$ and $g_n(Z_m) = 0.6382$. The Matskevich data closely follows an n value of 0.725. This also matches the high energy results of Gair and stopping power values. For this case $Z_m = 1.284$ and $g_n(Z_m) = 0.6552$. In view of our previous analysis we feel that these values best represent polymer emission data.

In those cases where the total yield σ is desired the backscatter η must be included. We found that for polymers containing H, C, N and O the energy dependence could be expressed by

$$\eta = 0.115 E_0^{-0.223} \quad (14)$$

with E_0 in keV.

Summary

For convenience we summarize here the essential relations required to reproduce the available polymer secondary emission data and to predict values for those yet to be studied.

Emission Coefficient

$$K = 10.64 (N/M) - 3.15$$

where N is the number of valence electrons in a repeating polymer unit (1,4,5,6 for H,C,N,O) and M is the gram molecular weight.

Energy at Maximum Yield

$$E_{om} = (K/12.09)^{0.580}$$

with E_{om} in keV.

Maximum Yield

$$\delta_m = 9.5 E_{om}$$

Yield as a Function of Incident Energy

$$\delta(E_0) = 1.526 \delta_m g_n(Z)$$

where

$$g_n(Z) = (1 - \exp(-Z^{1.725}))/Z^{0.725}$$

and

$$Z = 1.284 E_0 / E_{om}$$

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TABLE I
MAXIMUM POLYMER YIELDS AND RELATED BEAM ENERGIES

POLYMER	REF.	σ_m	δ_m	E_{om} (KeV)	δ_m/E_{om}
POLYETHYLENE	2	2.85	2.71	.250	10.8
POLYVINYLALCOHOL	2	2.6	2.47	.270	9.1
POLYAMIDE (NYLON)	2	2.6	2.42	.250	9.7
POLYMETHYL METHACRYLATE (LUCITE)	2	2.4	2.30	.240	9.6
POLYSTYRENE	2	2.07	1.90	.200	9.5
POLYSYTRENE	4	3.0	--	.250	
POLYETHYLENE TERPHTHALATE (MYLAR)	4	4.8	--	.175	
POLYETHYLENE TERPHTHALATE (MELINEX)	4	3.2	--	.250	
4-BROM-2,5-DIMETHYLSTYROL	2	1.9	1.75	.200	8.75
2,3-DICHLORO-4,5-DIMETHYLSTYROL	2	2.0	1.83	.200	9.15
POLYTETRAFLUOROETHYLENE (TEFLON)	2	2.35	2.12	.400	5.3
POLYTETRAFLUOROETHYLENE (TEFLON)	4	3.0	--	.300	
POLYIMIDE (KAPTON)	4	2.1	--	.150	

TABLE II
EMISSION COEFFICIENT K

POLYMER	FORMULA	K*
TEFLON	CF ₂	1.546
POLYETHYLENE	CH ₂	1.370
POLYVINYLALCOHOL	C ₂ H ₄ O	1.242
NYLON	C ₆ H ₁₁ ON**	1.148
LUCITE	C ₅ H ₈ O	1.115
POLYSTYRENE	C ₈ H ₈	0.907
MYLAR	C ₁₀ H ₈ O ₄	0.847
KAPTON	C ₂₂ H ₁₀ O ₅ N ₂	0.682

* For use in Eq. (2) with E₀ in keV

** The specific polyamide was not identified by Matskevich.
The formula presented here is that for the common Nylon 6.
Other Nylons yield a similar valence electron to mole weight ratio.

Fig. 1 The experimental Data of Matskevich² falls within a narrow range when plotted in reduced coordinates and is closely represented by the semiempirical model.

Fig. 2 Experimental results for polyethylene and lucite (polymethyl methacrylate, plexiglas, PMMA) from three different sources compared with calculated results using the semiempirical model.

Fig. 3 The Kapton yield obtained by Willis has a slope on this plot that departs markedly from that for all other polymers. The Mylar data has a reasonable slope but the yield at a given energy is higher than would be expected when compared with the Gair data.

Fig. 4 The coefficient K appears to be simply related to the composition of the monomeric unit in most polymers.