

A Stochastic Model for Predicting the Service Life of Photolytically Degraded Poly(methyl Methacrylate) Films

JONATHAN W. MARTIN, *Center for Building Technology, National Bureau of Standards, Washington, D.C. 20234*

Synopsis

A stochastic model has been proposed and partially validated for predicting the service life of a nominal population of polymethyl methacrylate films subjected to photolytic degradation. Here, service life is defined as the time after which an unacceptable portion of a nominal population of PMMA films subjected to photodegradation have failed; failure occurs when a performance property of the film falls below a predesignated minimum value. The stochastic model has two parts. The first part uses a Poisson distribution in computing the probability that exactly K photon related chain scissions will occur in the film in the interval $[0, t)$. The parameter of the Poisson distribution is made functionally dependent on temperature and the intensity of radiation absorbed. The second part determines the probability that a performance property will be greater than a minimum value after K chain scissions. This part is called the damage process. Together, the two parts of the model form a compound Poisson process. The main points of the models are validated against 25 published data sets. The plausibility of the Poisson process was substantiated for modeling the number of chain scissions occurring in the interval $[0, t)$. Also, it was demonstrated that the expected change in two performance properties of the films was functionally related to the expected number of chain scissions.

INTRODUCTION

When a polymeric component is exposed to the sun, it degrades. Degradation is the result of changes in one or more properties of the component. With continued exposure, these properties continue to degrade impairing the functioning of the component. When at least one of the important properties degrades pass a predesignated minimum value, the component is said to have failed. The time, corresponding to this first passage, is called the service life of the component (see Fig. 1).

For a nominal population of components made from the same polymer and exposed to the same environmental and operating conditions, one often observes a large variation in the times to failure. Since these observed times to failure often span several decades of time, service life predictions based on the mean time to failure have little practical value. For a given application and service environment, a better criterion for making service life predictions would be to find the maximum time beyond which a specified portion of the nominal population survives. This criterion is stated in a probabilistic format. This probability is represented in Figure 1 by $\bar{H}(t)$ (the shaded areas under the probability density functions) and can be computed from the parameters of the service life distribution.

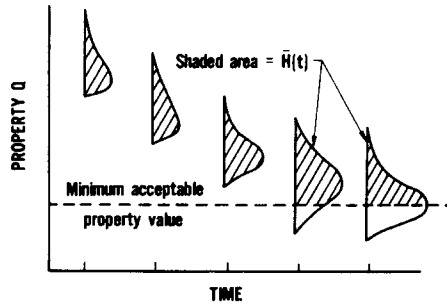


Fig. 1. Schematic of change in the property value of a component with exposure time to a photo-degradation source.

Traditionally, estimation of this probability, or, more importantly, of the parameters of the service life distribution, has been difficult. One reason is that the factors comprising a service environment vary widely from location to location both in their type and their intensity. For this reason, it is very important that the parameters of the service life distribution are made functionally dependent on the degradation variables. The most common experimental procedure for doing this is through the use of accelerated aging tests. Accelerated aging tests are laboratory experiments in which one or more of the factors encountered in a service environment (ultraviolet radiation, temperature, and moisture) are elevated to levels higher than normal. Accelerated aging tests are preferred to outdoor exposures because they are usually (1) less time-consuming, (2) less expensive, (3) capable of yielding results applicable to many different test locations, and (4) more valuable for isolating the effect of individual and combined degradation factors. Estimates of the parameters of the life distributions at these elevated levels are usually easy to obtain. Problems arise, however, in finding suitable mathematical models for making extrapolations to in-service conditions.²

Besides accounting for the variability in times to failure, the mathematical model used for making these extrapolations must account for the effects of individual and combined factors on the degradation of the component. It must also allow for more than one degradation mechanism. The complexity of this problem is recognized, particularly since in only a few cases is the effect of more than one degradation factor known.² Based on recently published research, a stochastic model is proposed for predicting the service life of polymethyl methacrylate (PMMA) subjected to photodegradation. The rate of degradation is made functionally dependent on temperature and the intensity of the radiation absorbed. This rate dependence is qualitatively justified on the basis of published results. The proposed model is partially validated against 25 data sets.

REVIEW OF PHOTODEGRADATION OF PMMA

At temperatures below 130°C, the photodegradation of PMMA is almost exclusively the result of random main chain scission.³⁻⁷ Crosslinking has not been observed to occur except in the presence of some sensitizers,^{8,9} and thermal

TABLE I
Published Quantum Yields of Main Chain Scission for Photodegradation of PMMA Films

Reference	Temp (°C)	Ambient atmosphere	Light source (nm)	Quantum yield	Material thickness (cm)
21	<40	Air	253.7	0.0245-0.0345	0.002
21	<40	Vacuum	253.7	0.03-0.0455	0.002
21	<40	Air	300	0.0051-0.0160	0.002
21	<40	Vacuum	300	0.0064-0.0121	0.002
29	25	Air	253.7	0.0093	0.0043
29	25	Vacuum	253.7	0.012	0.0043
10	150-195	Vacuum	253.7	0.1+	0.0012-0.022
4	25	Air	253.7	0.039	0.003
4	25	Vacuum	253.7	0.017	0.003
5	25	Vacuum	300-313	0.0023	0.008-0.009
23	25	Air	253.7	0.032	0.001
30	25	Nitrogen	253.7	0.005	0.001-0.006
6	25	Vacuum	253.7	0.05	0.005-0.01
2, 18	160	Vacuum	253.7	0.029-0.089	0.0003-0.0014
2, 18	170	Vacuum	253.7	0.070-0.229	0.0003-0.0014
2, 18	180	Vacuum	253.7	0.129-0.613	0.0003-0.0014
2, 18	190	Vacuum	253.7	0.188-0.817	0.0003-0.0014
2, 18	200	Vacuum	253.7	0.213-1.021	0.0003-0.0014
7	26	Air	253.7	0.0023	0.021-0.22
31	25	Air	253.7	0.0075	0.0003-0.003

degradation does not appear to be significant at these temperatures. For this reason, only equations having to do with random chain scission are reviewed.

For a photochemical process, the relationship between incident radiation and the frequency of occurrence of a particular process is given by the quantum yield. For chain scission, the quantum yield ϕ_{cs} is

$$\phi_{cs} = N_{cs}/I_a \quad (1)$$

where N_{cs} is the number of chain scissions per unit time and I_a is the number of quantum absorbed per unit time. Published values of the quantum yield of chain scission for PMMA are given in Table I. In almost every case, these quantum yield values were considered to be a constant. The value of N_{cs} is obtained from measurements of the number average molecular weight, viz.,

$$N_{cs} = (M_{n_0}/M_{n_t} - 1) \quad (2)$$

where M_{n_0} is the initial number average molecular weight and M_{n_t} is the number average molecular weight at time t . The number of quantum absorbed per unit time, I_a , on the other hand, is determined using the Lambert-Beer law, given by

$$\ln I/I_0 = -al \quad (3)$$

where¹⁰ I_0 is the radiation intensity at the surface of the film, I is the amount of radiation transmitted through the film, a is the absorption coefficient, and l is the film thickness. The intensity of radiation absorbed by the film is given by

$$I_a = I_0 - I \quad (4)$$

where both the amount of radiation absorbed, I_a , and the quantum yield of chain scission, ϕ_{cs} , are wavelength-dependent.

Given a specimen of thickness l absorbing I_a photons of wavelengths having sufficient energy required for chain scission (see Refs. 5, 11-13 for a discussion of a threshold wavelength), then the total number of chain scissions in time t for a block of material of unit area and thickness l is given by

$$I_a \phi_{cs} t = (M_{n_0}/M_{n_t} - 1) A \rho / M_{n_0} \quad (5)$$

where $A \rho / M_{n_0}$ is a scaling factor to convert the number of scissions per molecule to the total number of scissions in a volume of unit cross section and thickness l , ρ is the density of PMMA, having a value of 1.17 g/cm³, and A is Avogadro's number. In the case of monochromatic light, eq. (5) can be solved explicitly by experimentally determining the number of quantum absorbed, I_a , and substituting this value into eq. (1) and solving for quantum yield. In the case of polychromatic light, however, it is difficult to experimentally determine the relationship between the amount of radiation absorbed at each wavelength and the corresponding quantum yield of chain scission. In this case, the expected number of chain scissions per unit time, $I_a \phi_{cs}$, can be found by plotting the right hand side of eq. (5) vs. time.

With each chain scission, damage results in the film. Two indicators of damage, which will be used to demonstrate the service life prediction methodology, are changes in the number average molecular weight and the glass tran-

sition temperature. The mathematical expressions indicating change in these properties as a function of the number of chain scissions are now developed.

The initial number average molecular weight M_{n_0} is defined by

$$M_{n_0} = \sum n_i m_i / \sum n_i$$

where m_i is the molecular weight of a polymer molecule with degree of polymerization i and n_i is the number of molecules in the sample having degree of polymerization i ; therefore, $\sum n_i m_i$ is the total mass of the polymer and $\sum n_i$ is the total number of polymer chains in the sample.

After K chain scissions have occurred in the film, the new number average molecular weight M_{n_k} is given by

$$M_{n_k} = \sum n_i m_i / (\sum n_i + K) \quad (6)$$

Assuming that little or no mass is loss as the material degrades, eq. (6) can be simplified to

$$M_{n_k} = A_1 / (A_2 + K) \quad (7)$$

where A_1 is a constant and A_2 is a function of the initial molecular weight M_{n_0} .

Another indicator of damage to the film is a change in the glass transition temperature. Beevers and White¹⁴ give an equation of the form

$$T_g = T_g^\infty - CM_n^{-1} \quad (8)$$

for relating glass transition temperature to number average molecular weight. Here T_g^∞ is the glass transition temperature for a PMMA polymer having infinite molecular weight (published value 387°K¹⁴ and C is an empirical constant (published value 2.1×10^5 14). Substituting eq. (7) into eq. (8), one obtains

$$T_g = T_g^\infty - C(A_2 + K)/A_1 \quad (9)$$

which is linear with respect to total number of chain scissions.

In the next section, a stochastic model for the photodegradation of PMMA is presented incorporating the above facts. The objective of this section is to develop an expression for the probability, $\bar{H}(t)$, that an important property of PMMA is greater than a predesignated minimum value, when PMMA is subjected to a photolytic source for an interval t .

STOCHASTIC MODEL FOR THE PHOTODEGRADATION OF PMMA

In a typical photolysis experiment, a film is positioned at normal incidence and at a fixed distance from a radiation source. If the radiation intensity at the surface of the exposed film is I_0 , then $I_0 t$ photons strike the surface of the film in the interval $[0, t)$. Of these photons, only a fraction, p , is actually absorbed by the film. This fraction is equal to $1 - I/I_0$. The event of a photon absorption can be considered as a Bernoulli trial¹⁵; the number of photons absorbed by the film, N_t , has a binomial distribution with an expected value, $pI_0 t$; that is,

$$\text{Prob}(N_t = n) = b(n; I_0 t, p)$$

Here, the number of photons impacting the film is very large and p is small; therefore, the binomial distribution can be approximated by the Poisson distribution with almost no error; thus,

$$b(n; I_0t, p) \approx P(n; pI_0t)$$

where

$$P(n; pI_0t) = e^{-pI_0t} (pI_0t)^n / n! \quad \text{for } n = 0, 1, 2, \dots \quad (10)$$

Although N_t photons are absorbed, only a fraction of these actually result in chain scissions. This fraction is the average quantum yield of main chain scission, ϕ_{cs} [see eq. (1)]. The magnitude of the quantum yield is controlled to a large extent by a mixture of two processes—a nonphotooxidative process and a photooxidative process.³ For thin films and low temperatures, the rate of photodegradation appears to be linear with time (references in Table I); accordingly, the expected number of chain scissions in the interval $[0, t)$ is given by

$$E(K) = p\phi_{cs}I_0t \quad (11)$$

At low temperatures, the mechanisms causing photodegradation have been identified by Fox et al.⁴ and Gupta.⁶ These reactions are characterized as being nonphotooxidative and as having low quantum yields. As the film thickness and temperature increase, however, photooxidation becomes increasingly important.³ At sufficiently high temperatures (temperatures close to the glass transition temperature) and radiation intensities, the diffusion of oxygen limits the rate of photooxidation in PMMA.³ Even at these high temperatures, however, a mixture of the photooxidative and nonphotooxidative processes is present. For this mixture, it has been shown by Fukushima¹⁶ that a power law adequately models the number of chain scissions as a function of time, that is,

$$E(K) = p\phi_{cs}I_0t^m \quad (12)$$

where from theoretical considerations $0.5 < m < 1.0$. Equation (11) is a special case of eq. (12). In eq. (12), the exponent should have a value close to 0.5 when photooxidation predominates and the diffusion of oxygen obeys Fick's law.³ The exponent should have a value close to 1 for thin films when nonphotooxidative processes dominate photodegradation. The adequacy of the power law for predicting the number of chain scissions as a function of time is tested in the Results and Discussion section.

In eq. (12), the time axis is transformed using a power law. Since this is a homogeneous transformation, the Poisson probability distribution is preserved. Therefore, the probability that exactly K chain scissions occur in the time interval $[0, t)$ is given by

$$P(k; \lambda\tau) = e^{-\lambda\tau} (\lambda\tau)^k / k! \quad \text{for } k = 0, 1, 2, \dots \quad (13)$$

where

$$\lambda\tau = p\phi_{cs}I_0t^m$$

and

$$\tau = t^m$$

As before, the expected number of chain scission and the variance of that number are

$$E(K) = \lambda\tau \quad (14)$$

and

$$\text{var}(K) = \lambda\tau \quad (15)$$

Note that the variance increases with exposure time. For consistency, the symbol t is used for time in the remainder of this paper, since the Poisson distribution is preserved for a homogeneous transformation of the time axis.

As the temperature and intensity of radiation absorbed are increased, the Poisson parameter λ must be modified to reflect changes in the quantum yield of main chain scission. (The fraction of photons absorbed by the film, p , is assumed to remain constant). It is hypothesized that this relationship is adequately described by

$$\lambda = \exp\left[-\frac{E(T - T_0)}{RTT_0}\right] \left(\frac{I_\alpha}{I_a}\right)^n \Lambda_0 \quad (16)$$

where the first term is the Arrhenius acceleration factor and the second term is an acceleration factor for intensity of radiation absorbed. Also, T_0 is a reference absolute temperature, T is an absolute temperature, I_α is a reference intensity of radiation absorbed, I_a is an intensity of radiation absorbed, Λ_0 is the expected number of main chain scissions occurring at the reference temperature T_0 and the reference intensity of radiation absorbed level I_α , and n is an empirical constant which for transparent films, appears to have a value of 1.^{2,17-19} For opaque films, n appears to have a value less than 1.¹⁷ E is an activation energy, and R is the gas constant.

Equation (16) is consistent with Dan and Guillet's²⁰ equation for the effect of temperature on quantum yield for the photodegradation of a copolymer of PMMA and Koike and Tanayka's¹⁷ equation for combined temperature and radiation on the photodegradation of different polymers. It is also qualitatively consistent with the experimental results of Dickens et al.³ for the photodegradation of PMMA. At low temperatures, Dickens et al. attributed the low quantum yield of main chain scission and the almost uniform degradation through the thickness of the film to the efficiency of the cage effect. As the temperature increases, however, more radicals are able to escape the cage and react with oxygen, producing alkoxy radicals. Photooxidation takes place through a β -scission of these alkoxy radicals. The proportional increase in the number of radicals escaping the cage and reacting with oxygen as the temperature increases is modeled in eq. (16) by the Arrhenius acceleration factor. The effect of an increase in intensity of radiation absorbed is to increase the number of free radicals. At low temperatures, an increase in the intensity is directly related to an increase in the number of chain scissions; hence, the exponent in eq. (16) has a value of one.^{2,4,18,19} At sufficiently high intensities of radiation absorbed and at sufficiently high temperatures, however, initiation of new radicals is no longer rate limiting. Instead, the diffusion of oxygen becomes rate limiting.³ In this case, the value of the exponent in eq. (16) has a value less than 1.

To account for variability in the properties of the components, the property value Q is considered to be a random variable. The probability density function of this property, prior to exposure to a photodegradation source, is given by $f_0(q)$. After K chain scissions, the new probability density function for the property

Q is denoted by $f_K(q)$ for $K = 0, 1, 2, \dots$. From the standpoint of service life prediction, the probability that the property value for a film is greater than a specified minimum value q after the first K chain scissions is given by

$$\bar{F}_K(q) = \int_q^\infty f_K(u) du \quad (17)$$

where

$$1 \geq \bar{F}_0(q) \geq \bar{F}_1(q) \geq \dots \geq \bar{F}_{K-1}(q) \geq \bar{F}_K(q) \quad (18)$$

for all possible K . Note that eq. (18) allows for the film to be in a failed state at the time of installation and requires that damage be accumulated as the number of chain scissions increases; i.e., the property value cannot improve with increasing chain scissions. Equations (17) and (18) give the probability of surviving the first K chain scissions. The probability that the film is in a failed state after the first K chain scissions is given by

$$F_K(q) = 1 - \bar{F}_K(q) \quad (19)$$

If chain scissions occur randomly in time as events in a Poisson process, then the probability of exactly k chain scissions occurring in a time period of length t is given by eq. (13), and the corresponding probability that the property value of interest is greater than the minimum value is given by eq. (17). The total probability $\bar{H}(t)$ that the material survives beyond time t is

$$\bar{H}(t) = \sum_{k=0}^{\infty} \bar{F}_k(q) \frac{e^{-\lambda t} (\lambda t)^k}{k!} \quad (20)$$

for $\lambda > 0$ and $t \geq 0$. Equation (20) defines a compound Poisson process and is equal to the shaded areas under each probability density function in Figure 1. An excellent review of the properties of the compound Poisson process is given by Esary, Marshall, and Proschan.²¹ Equation (20) is of interest to in-service life prediction because it directly computes the probability of survival for photolytically degraded material exposed for a time t . More importantly, the model can be extended to include changes in the intensity of the degradation factors as a function of time; such a model is termed a cumulative damage model. This is an important attribute of the compound Poisson model, because the intensity of the degradation factors varies naturally with the diurnal cycle.

RESULTS AND DISCUSSION

The major objectives of this paper are to demonstrate the plausibility of the Poisson process [eq. (13)] for modeling the arrival of bond rupture-causing photons and to substantiate the statement that the expected damage to the film is only a function of the number of chain scissions. The effect of temperature and intensity of radiation absorbed on the expected number of chain scissions [eq. (16)] and the distributional form of the damage function $\bar{F}_K(q)$ [eq. (17)] could not be validated due to the lack of published data.

The data for validating eq. (13) and the assumption that damage to the film is only a function of the number of chain scissions comes from three sources: (1) Abouelezz and Waters,²² (2) Abouelezz and Waters,²³ and (3) Shultz.⁷ Altogether, 25 data assets were used. (Shultz's film D data were not used in the

TABLE II
Summary Description of Data Sets Used in Validation of the Stochastic Model

Data set	Reference	Initial no. avg mol wt	Initial wt avg mol wt	Thickness (cm)	Temp (°C)	Ambient atmosphere	Light source (nm)	Number specimens
1	Abouelezz ²¹	152,000	189,000	0.002	<40	Vacuum	253.7	10
2	Abouelezz ²¹	152,000	189,000	0.002	<40	Air	253.7	10
3	Abouelezz ²¹	152,000	189,000	0.002	<40	Vacuum	300	9
4	Abouelezz ²¹	152,000	189,000	0.002	<40	Air	300	9
5	Abouelezz ²²	152,000	189,000	0.002	<40	Air	300 Pyrex filter	5
6	Abouelezz ²²	152,000	189,000	0.002	<40	Air	300	5
7	Abouelezz ²²	152,000	189,000	0.002	<40	Air	Flood lamp	7
8	Abouelezz ²²	152,000	189,000	0.002	<40	Air	Pyrex filter	5
9	Abouelezz ²²	152,000	189,000	0.002	<40	Air	436	5
10	Abouelezz ²²	152,000	189,000	0.002	<40	Air	546	5
11	Abouelezz ²²	152,000	189,000	0.002	<40	Air	Xenon, IR filter	7
12	Abouelezz ²²	152,000	189,000	0.002	<40	Air	Xenon, borosilicate	9
13	Abouelezz ²²	197,000	248,000	0.002	<40	Air	253.7	10
14	Abouelezz ²²	197,000	248,000	0.002	<40	Vacuum	253.7	10
15	Abouelezz ²²	197,000	248,000	0.002	<40	Air	300	9
16	Abouelezz ²²	197,000	248,000	0.002	<40	Vacuum	300	9
17	Abouelezz ²²	197,000	248,000	0.002	<40	Air	300, Pyrex filter	5
18	Abouelezz ²²	197,000	248,000	0.002	<40	Air	300	5
19	Abouelezz ²²	197,000	248,000	0.002	<40	Air	Flood lamp, Pyrex filter	7
20	Abouelezz ²²	197,000	248,000	0.002	<40	Air	436	5
21	Abouelezz ²²	197,000	248,000	0.002	<40	Air	546	5
22	Abouelezz ²²	197,000	248,000	0.002	<40	Air	Xenon, IR filter	7
23	Shultz ⁷	4,380,000	8,100,000	0.0207	<40	Air	Xenon, borosilicate filter	9
24	Shultz ⁷	2,920,000	5,400,000	0.107	<40	Air	253.7	10
25	Shultz ⁷	4,420,000	8,200,000	0.22	<40	Air	253.7	8

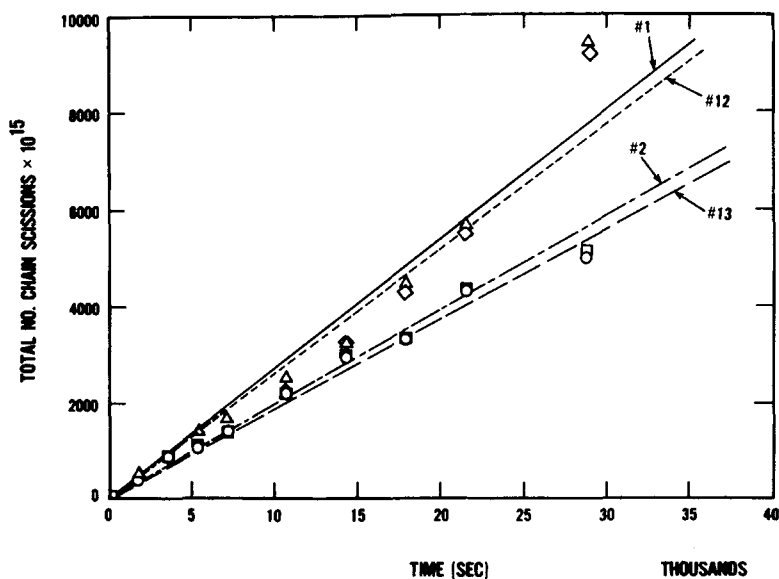


Fig. 2. Number of bond ruptures vs. exposure time for data sets 1 (Δ), 2 (\square), 12 (\diamond), and 13 (\circ).

analysis.) The 25 data sets differ from each other by one or more of the following: (1) initial molecular weight, (2) radiation source, (3) ambient environment, and (4) film thickness (see Table II). Also different among the data sets was the method used in measuring the average molecular weights. The measurements in Refs. 22 and 23 were made using a gel permeation chromatograph. A viscometer was used in Ref. 14. For photolytically degraded thick films, errors arise in estimating the number average molecular weight from the viscosity average molecular weight.^{24,25} These estimation errors arise because the number of photons absorbed varies with film depth. To compensate for this variation, a correction factor is commonly applied. For Shultz's data, Gardner and Epstein's²⁵ correction factor was used when computing number average molecular weights.

To validate the statement that the Poisson process adequately describes the number of chain scissions in the interval $(0, t]$, a simple check was made. For nonoverlapping time intervals, the Poisson distribution may be used if the expected number of chain scissions does not depend on previous history and if the expected number of chain scissions is only a function of the length of the interval times a constant²⁶; that is,

$$E[K_{t+s} - K_t | K_\mu; \mu \leq t] = \lambda s \quad (21)$$

where $t, s \geq 0$ and are intervals of time. Equation (21) is used as the basis for model validation. As Cinlar²⁶ points out, eq. (21) is the simplest qualitative characterization of the Poisson process. It is especially useful here, because the more fundamental properties of the Poisson process cannot be experimentally validated and strong *a priori* evidence exists suggesting that the number of chain scissions in any future time interval is independent of past history. This *a priori* evidence comes from the success of the Poisson processes for modeling the arrival

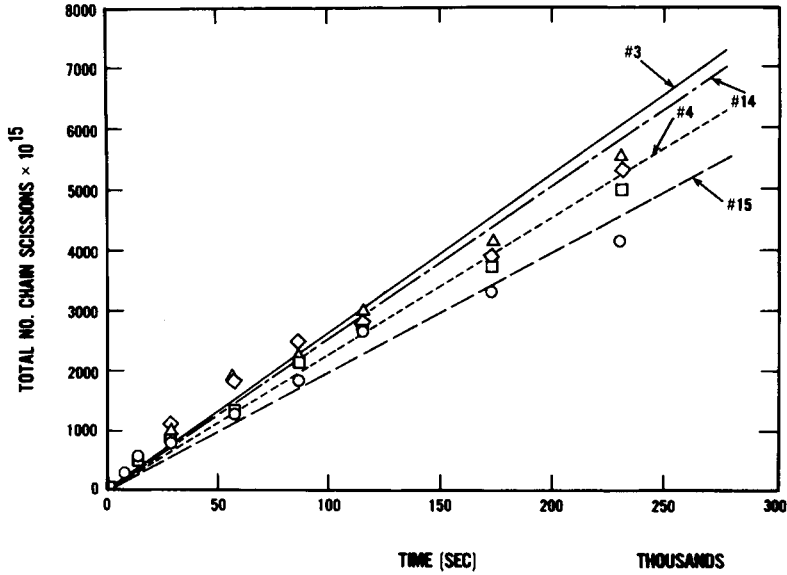


Fig. 3. Number of bond ruptures vs. exposure time for data sets 3 (Δ), 4 (□), 14 (◇) and 15 (○).

of electromagnetic radiation in a large number of other processes including health physics,^{27,28} electronics,²⁹ and physics.^{1,30}

Abouelezz and Waters' number of chain scissions versus exposure time data is plotted in Figures 2-6. Shultz's data are plotted in Figures 7 and 8. Abouelezz and Waters' films were very thin (0.002 cm); therefore, by eq. 11 and previous empirical evidence (see the references given in Table I), one would expect the

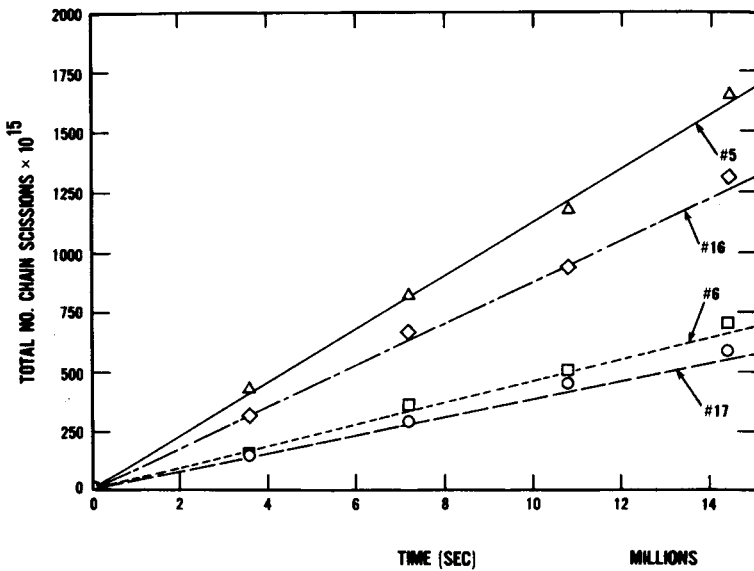


Fig. 4. Number of bond ruptures vs. exposure time for data sets 5 (Δ), 6 (□), 16 (◇), and 17 (○).

TABLE III
Expected Number of Chain Scissions/s for All 25 Data Sets

Data set	Power law exponent m	Thickness (cm)	Expected number chain scissions/ $s \cdot \text{cm}^3$ λ	Correlation coefficient r
1	1.0	0.002	2.70×10^{14}	0.990
2	1.0	0.002	1.98×10^{14}	0.997
3	1.0	0.002	2.64×10^{13}	0.998
4	1.0	0.002	2.32×10^{13}	0.999
5	1.0	0.002	1.14×10^{11}	0.999
6	1.0	0.002	4.79×10^{10}	0.999
7	1.0	0.002	2.04×10^{11}	0.999
8	1.0	0.002	3.10×10^{10}	0.994
9	1.0	0.002	2.52×10^{10}	0.996
10	1.0	0.002	1.08×10^{11}	0.997
11	1.0	0.002	1.06×10^{11}	0.999
12	1.0	0.002	2.62×10^{14}	0.990
13	1.0	0.002	1.93×10^{14}	0.997
14	1.0	0.002	2.57×10^{13}	0.996
15	1.0	0.002	2.08×10^{13}	0.996
16	1.0	0.002	8.97×10^{10}	0.999
17	1.0	0.002	4.13×10^{10}	0.999
18	1.0	0.002	1.59×10^{10}	0.999
19	1.0	0.002	2.32×10^{10}	0.996
20	1.0	0.002	1.98×10^{10}	0.997
21	1.0	0.002	8.32×10^{10}	0.997
22	1.0	0.002	8.69×10^{10}	0.999
23	0.91	0.0207	2.00×10^{14}	0.982
24	0.93	0.107	9.31×10^{14}	0.993
25	0.50	0.220	3.61×10^{15}	0.988

average number of chain scissions to be linear with time. This appears to be an adequate model since the correlation coefficients, which give a measure of the goodness of fit of a proposed model, are all greater than 0.99 (Table III). Deviations from the proposed model do occur after very long exposure times. For data sets 1 and 12, the observed number of chain scissions is greater than expected (see Fig. 2). For data sets 2 and 13, the observed number of chain scissions is less than expected (see Fig. 2). These deviations are consistent with the model, however, since the variance [eq. (15)] increases with increasing exposure time.

Shultz's films (data sets 23–25) were between 10 and 110 times thicker than those used by Abouelezz and Waters. With increasing film thickness, diffusion processes begin to dominate the photodegradation process. By eq. 12, the mixture of photodegradation and diffusion process can be adequately modeled using a power law. A power law fit, using least-square analysis, was made to data sets 23, 24, and 25. The results are shown in Figures 7 and 8. As expected, the exponent for the power law falls between 0.5 and 1.0 (see Table III). With increasing thickness, the exponent tends toward a value of 0.5. Again, correlation coefficients for data sets 23–25 were high indicating that power law adequately describes the arrival of chain scission causing photons. Since both eqs. (11) and (12) are linear with time and appear to be adequate models for predicting the

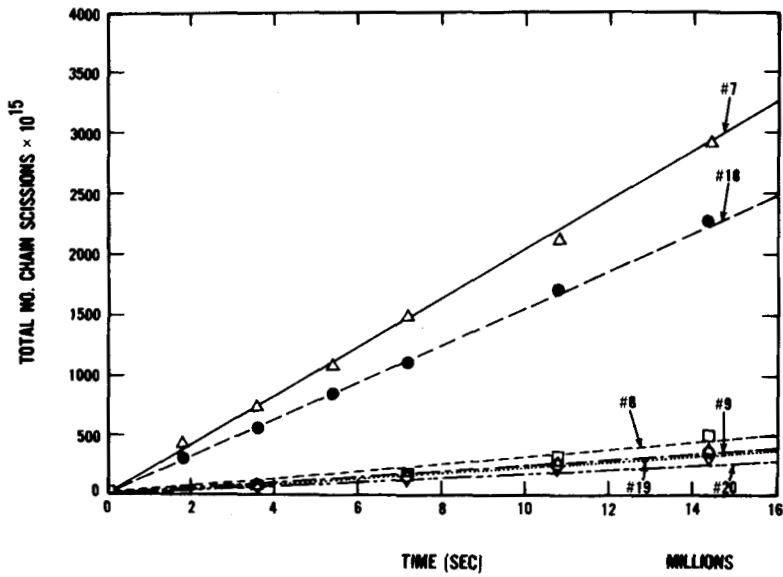


Fig. 5. Number of bond ruptures vs. exposure time for data sets 7 (Δ), 8 (\square), 9 (\diamond), 18 (\bullet), 19 (\circ) and 20 (∇).

number of chain scissions as a function of time for thin and thick specimens, eq. (21) is satisfied; hence, the Poisson model is substantiated. The slopes of the regression lines in Figures 2-8 are equal to the expected number of chain scissions per unit time [λ in eq. (13)]. The values of λ are tabulated in Table III for all data sets.

Two indicators of damage have been used in this paper—changes in the number average molecular weight and in the glass transition temperature. These

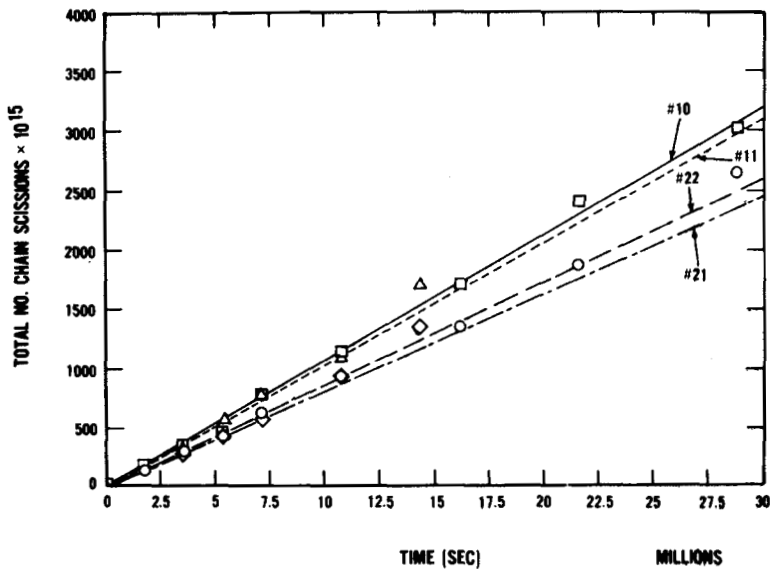


Fig. 6. Number of bond ruptures vs. exposure time for data sets 10 (Δ), 11 (\square), 21 (\diamond), and 22 (\circ).

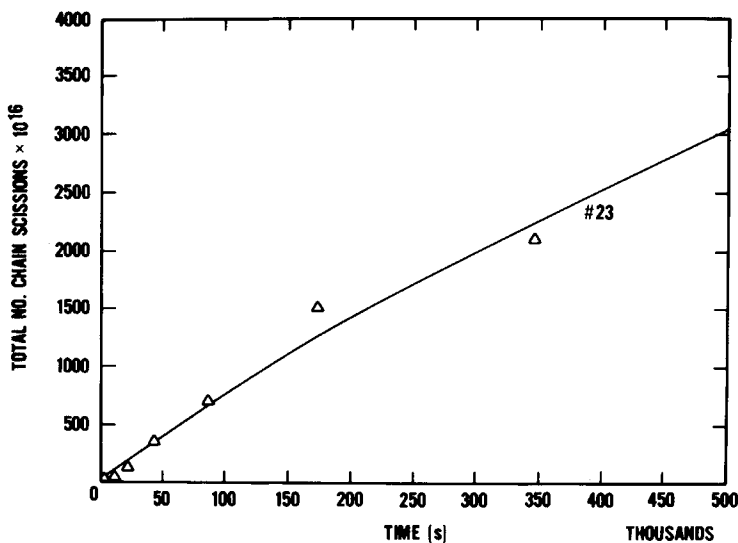


Fig. 7. Number of bond ruptures vs. exposure time for data set 23.

indicators were chosen for the demonstration of the service life prediction methodology. In practice, damage indicators should be selected on the basis of their ability to predict performance. From eq. (20), the distributional form of both properties [eq. (17)] must be known. As mentioned before, these distributions are not known, as yet, due to lack of published data. The expected value of each of these properties as a function of the number of chain scissions is given by eqs. (8) and (9). These expectations are fitted to the observed values in Figures 9 and 10. The expected value of the number average molecular weight is given approximately by

$$E[M_{nk}] \simeq A_1 / (A_2 + \lambda t) \quad (22)$$

and the expected value of the glass transition temperature, assuming Beevers and White's model is correct, is given by

$$E[T_{gk}] \simeq T_g^\infty - C \left(\frac{A_2 + \lambda t}{A_1} \right) \quad (23)$$

The number average molecular weight is plotted as a function of exposure time in Figure 9 for Abouelezz and Waters' ^{22,23} data sets 1, 2, 12, and 13. The expected number average molecular weight curves [eq. (22)] are superimposed on these plots using λ values given in Table III. Plots for the other 21 data sets are just as good.

Changes in glass transition temperature as a function of exposure time are plotted in Figure 10 for data sets 1, 2, 12, and 13. The expected glass transition temperature curves [eq. (23)] are superimposed in Figure 10 using the λ values tabulated in Table III. The fit of eq. (23) to the data was not as good as expected. A much better fit was obtained when glass transition temperature was directly related to the number average weight; i.e., $T_g = T_g^\infty - CM_n$ as opposed to eq. (5). Nevertheless, eq. (23) appears to be an adequate predictor of change in glass transition temperature.

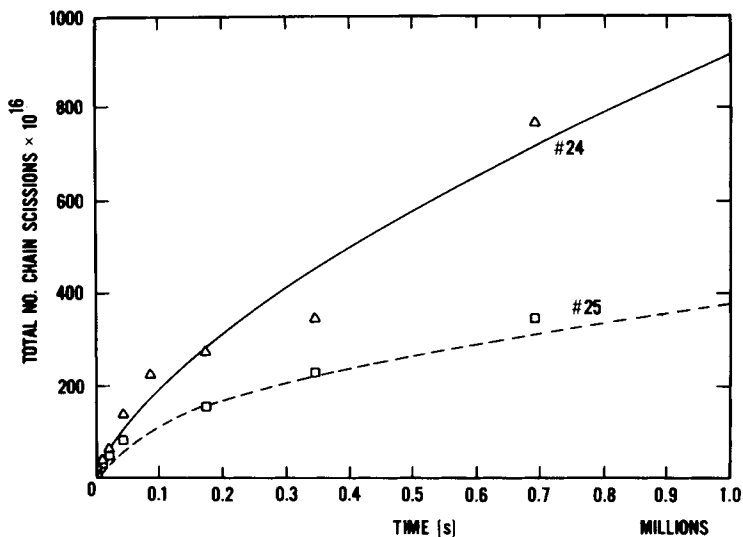


Fig. 8. Number of bond ruptures vs. exposure time for data sets 24 (Δ) and 25 (\square).

SUMMARY AND CONCLUSIONS

A stochastic model [eq. (20)] has been proposed and partially validated for predicting the service life of a nominal population of poly(methyl methacrylate) films subjected to photolytic degradation. Here, service life is defined as the time after which an unacceptable proportion of a nominal population of PMMA films subjected to photodegradation have failed; failure occurs when a performance property of the film falls below a predesignated minimum value. The

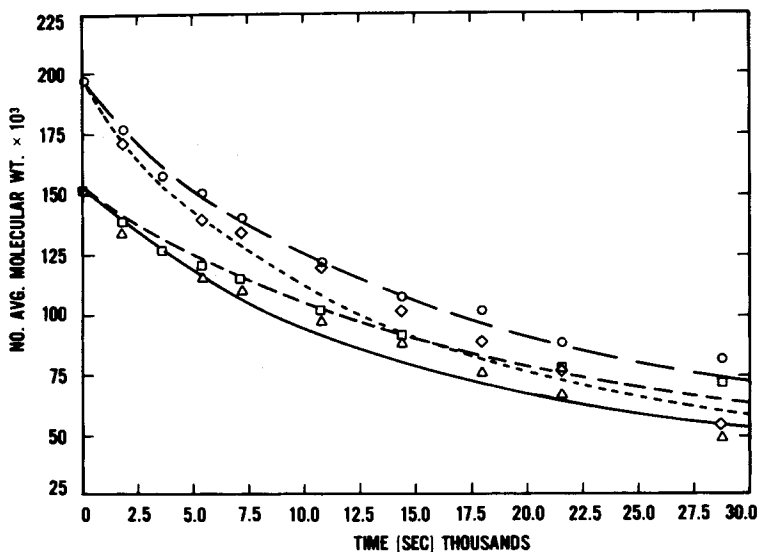


Fig. 9. Change in weight average molecular weight as a function of the number of bond ruptures for data sets 1 (Δ), 2 (\square), 12 (\diamond), and 13 (\circ).

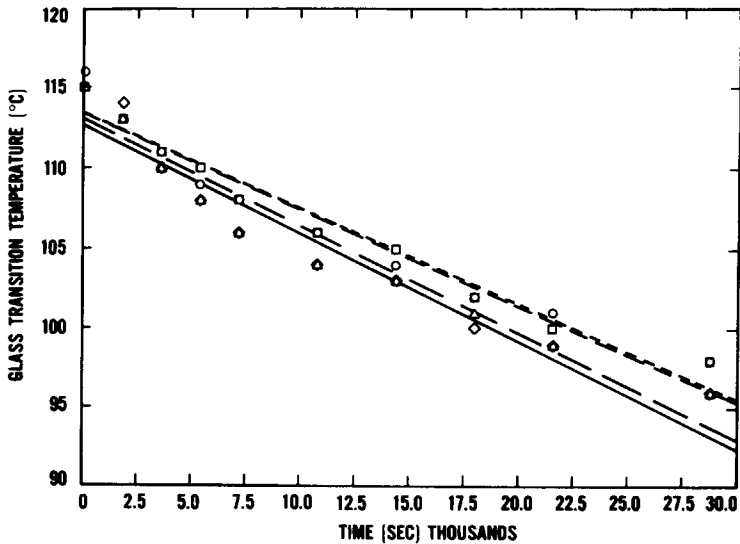


Fig. 10. Change in glass transition temperature as a function of the number of bond ruptures for data sets 1 (Δ), 2 (\square), 12 (\diamond) and 13 (\circ).

stochastic model has two parts. The first part uses a Poisson distribution in computing the probability that exactly K photon related chain scissions will occur in the film in the interval $[0, t)$. This part is called the arrival process. The second part determines the probability that a performance property will be greater than a minimum value after K chain scissions. This part is called the damage process. Together, the two parts of the model form a compound Poisson process.

For service life prediction, the proposed stochastic model is attractive for several reasons:

1. The parameters of the compound Poisson process are expressed in terms of the physics of failure of the polymer.

2. The arrival process only models those photon absorptions resulting in chain scissions; other nonchain scission causing processes are ignored. This economy greatly reduces the number of rate constants which would otherwise have to be estimated.

3. The rate of chain scissions is made a function of the temperature and irradiance levels.

4. Damage to the film can be any of a wide range of possible performance properties. It is necessary, however, that changes in performance be related to main chain scissions and that damage increases with an increasing number of chain scissions.

5. Finally, the stochastic model can be extended to include cumulative damage effects; i.e., it permits changes in the intensity of the degradation factors over time. This is an important feature of the compound Poisson model because the intensity of almost all weathering factors varies with the diurnal cycle.

In this paper, the entire model could not be validated due to the unavailability of suitable published data. Twenty-five published data sets were available, however, to verify the main points of the model. The plausibility of the Poisson

process was validated for modeling the number of chain scissions occurring in the interval $[0, t)$. Also, it was demonstrated that the expected change in two performance properties of the films were functionally related to the expected number of chain scissions. In on-going research at the National Bureau of Standards, a more extensive experiment is being conducted to provide data to validate the entire model.

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APPENDIX: NOMENCLATURE

Abbreviations

$b(k;n,p)$	binominal distribution with parameters n and p
E	mathematical expectation
$f_K(q)$	probability density function for critical property q after K chain scission
$F_K(q)$	cumulative distribution function for critical property q after K chain scissions
$\bar{F}_K(q)$	probability that critical property q has a value greater than a predesignated minimum value after K chain scissions
$\bar{H}(t)$	reliability or the probability the material survives beyond time t
\ln	natural logarithm
$P(k;\lambda)$	Poisson distribution with parameter λ
$\text{Prob}(-)$	probability of the event described within parentheses
var	mathematical variance

Symbols

λ	Poisson parameter for average number of main chain scissions per unit time
Λ_0	average number of main chain scissions per unit time at reference temperature T_0 and reference intensity radiation of absorption, I_a
ρ	density of PMMA
ϕ_{cs}	quantum yield of main chain scission
a	absorption coefficient
A	Avogadro's number
A_1, A_2	empirical constants
c	empirical constant
E	activation energy
I	radiation intensity transmitted through the film
I_0	radiation intensity at surface of film
I_α	reference intensity of radiation absorbed
I_a	intensity of radiation absorbed or number of quantum absorbed per unit time
k	observed number of main chain scissions
K	number of main chain scissions random variable
l	thickness of film
p	probability of a photon being absorbed
m	power law exponent
M_{n_0}	initial number average molecular weight
M_{nk}	number of average molecular weight after k main chain scissions
M_{n_t}	number average molecular weight after exposure to a photolytic source for an interval t
m	intensity of radiation absorbed acceleration factor exponent
N_{cs}	number of chain scissions per unit time
N_t	number of photon absorptions in the interval t

R	gas constant
t	time
T	absolute temperature
T_0	reference absolute temperature
T_g	glass transition temperature
T_g^∞	glass transition temperature for PMMA having an infinite molecular weight

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