Modeling the Degradation of Natural Rubber Male Condoms

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ABSTRACT: Most condom manufacturers claim a 5 year shelf-life for their products; however, condoms can decay much more rapidly than the reported shelf-life would suggest, because of the uncontrolled storage conditions. For this reason, development of mathematical model to predict condom shelf-life as a function of storage conditions can be very useful. In this work, six brands of condoms were aged under subtropical ambient conditions for 5 years and under accelerated conditions at four temperatures for various times. The changes in burst pressure and burst volume were used as the main indicators of product degradation. Experimental data were analyzed and two mathematical models (both based on the reparameterized Arrhenius equation) were proposed to describe the obtained data. It is shown for the first time that it is possible to estimate and predict the degradation of natural rubber condoms with confidence with the help of the proposed models, based on data obtained from accelerated degradation experiments, provided that different activation energies are used for the burst pressure and volume.
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Key words: condoms; natural rubber; accelerated aging; lifetime prediction; modeling

INTRODUCTION

In the late 1980s, HIV (Human Immunodeficiency Virus) became a major public health issue and it became clear that consistent condom use is very effective in preventing its transmission.[1–4] Besides, condoms are also effective to prevent other sexually transmitted infections.[5] As a result, many international aid agencies supply large quantities of condoms to developing countries. Approximately 2 billion condoms are distributed by nonprofit organizations each year, largely to limit the spread of HIV.[6] The distribution pipelines are long and complex, involving tropical sea voyages, storage on open wharves, truck transport and storage in suboptimal warehouses. It can take some years from the time of manufacture for a condom to reach the end user. It is therefore a major public health goal to guarantee that condoms are still reliable when they reach the end user.

The combination of high force at break and elasticity of good quality condoms lead to very low rates of failure in use. However, it is widely known that the initial properties of rubber decay over time. As a consequence, the elasticity and strength will eventually drop to undesired low values. Tests conducted by Family Health International (FHI) indicated that there was a significant increase in risk of breakage in condoms more than 2 years old.[7] Aging could be correlated with a drop in burst properties, and it is logical to assume that the change in physical properties, rather than age alone, is a more fundamental indicator of deterioration.

The Arrhenius equation has been widely used to study the deterioration of rubber articles, including condoms and medical gloves. Although its use is still accepted for gloves, more critical evaluation has been addressed to its application to condoms, especially by the ISO committee responsible for condom standards. The 2002 edition of ISO 4074 (condoms)[8] combined the Arrhenius equation with a time-shift factor to determine shelf life as a function of the storage temperature and time. The proposed approach is based on the use of a time-temperature factor to correct the shelf live, as evaluated at standardized conditions, assuming constant activation energy. An alternative semigraphical method is described in the ISO 11346.[9] However, data obtained from a number of manufacturers revealed that these approaches did not approximate real time behavior.

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Based on the previous discussion, the main objective of the present manuscript is to develop a methodology for determination of shelf time of rubber male condoms as a function of storage conditions. As the properties of different products are not necessarily similar, it is assumed that the proposed methodology must rely on independent experimental characterization of product performances. For this reason, in the this work six brands of condoms were aged under subtropical ambient conditions for 5 years and under accelerated conditions at four temperatures for various times. Then, two empirical models (both based on the reparameterized form of the Arrhenius equation) were developed and validated to predict rubber male condom degradation, based on inflation tests made over a period of 5 years.

The reparameterization of the Arrhenius equation reduces the correlation between the estimated parameters, reduces the computational effort required to minimize the objective function and leads to smaller confidence regions of final parameter estimates and model predictions.[10–12] Consequently, parameter uncertainties can be reduced and more precise shelf life predictions can be obtained. Additionally, the proposed analysis allows for proper characterization of parameter uncertainties, which cannot be performed with simplified methods based on graphical interpretation of available data.[8,9] Finally, the analysis performed here also allows for precise definition of confidence regions of model predictions, which have been neglected in previous studies.

The models were used to fit experimental values obtained for the individual condom lots and for the whole set of experiments. A database of burst pressure and volume (inflation test) results was analyzed statistically using STATISTICA.[13] Model parameters were estimated with the least-squares technique. A combination of the Hooke-and-Jeeves and the quasi-Newton methods was used for minimization of the objective function. The combination of these two techniques is convenient because the Hooke-and-Jeeves method is not very sensitive to initial guesses, making the first numerical iterations more robust, and the quasi-Newton method converges fast when good initial guesses become available after the first numerical iterations.[14–16]

Although the proposed methodology comprises more sophisticated experimental and numerical analyses, it is shown in the following sections that it can be easily performed by rubber male condom manufacturers for precise determination of condom shelf life at different storage conditions. Besides, it is shown that the proposed methodology leads to characterization of individual activation energies for both burst pressure and volume degradation, as the performances of different products are not necessarily the same.

TABLE I
Condom Types Used

Condom	Lubrication	Package	Shelf-life (years)
A1[a]	Silicone fluid	Square aluminum	3
A2	Silicone fluid	Square aluminum	3
A3[a]	None	Square aluminum	3
B1	Silicone fluid	Square aluminum	3
B2[a]	Silicone fluid	Square aluminum	3
B3[a]	Silicone fluid	Square aluminum	3
C1[a]	None	Square aluminum	3
C2	Silicone fluid	Square aluminum	3
C3[a]	Silicone fluid	Square aluminum	3
D1[a]	Silicone fluid	Square plastic	3
D2	Silicone fluid	Square plastic	3
D3[a]	Silicone fluid	Square plastic	3
E1[a]	Silicone fluid	Square aluminum	5
E2[a]	Silicone fluid	Square aluminum	5
F1	Silicone fluid	Square aluminum	5
F2	Silicone fluid	Square aluminum	5
F3	Silicone fluid	Square aluminum	5

[a] Oven aged.

EXPERIMENTAL

Materials—Condoms

Seventeen lots of natural rubber condoms from six different manufacturers (coded A to F) produced between June 1999 and November 2000 were used to perform the experiments. All samples were parallel-sided naturally colored condoms, with a width of approximately 52 mm. Most lots were lubricated with silicone fluid. Samples were packed in square aluminum foil packages, with the exception of brand D, which was packed in plastic packages. Table I presents the types and some characteristics of the samples used. All samples were aged under ambient conditions. Samples marked with "a" were also aged under accelerated conditions at elevated temperatures.

Real time storage conditions

Samples were stored in cartons in a storeroom in Rio de Janeiro for 5 years. Storage temperature was monitored on a daily basis, three times a day. The average storage temperature was 27°C, with extreme temperatures of 17°C in winter and 42°C in summer.

Oven aging

Samples from the 10 lots marked with "a" in Table I were aged in a fan-forced oven inside their individual packages. Temperatures were kept constant

TABLE II
Experimental Design

	Aging times (days)													
T (°C)	2	3	7	9	14	21	28	42	56	70	84	97	140	182
50			X		X		X	X	X	X	X	X	X	X
60					X		X	X	X	X	X			
70	X		X		X	X	X	X						
80		X	X	X	X									

(±1°C) at 50, 60, 70, and 80°C, for intervals of 2 to 182 days (depending on the aging temperature) as shown in Table II.

Test protocol

Thirty real time samples were inflation-tested at intervals of 4 months over a period of 5 years. The 5 year period was chosen because it is the longest shelf-life claim permitted by the ISO standard.[8]

For all oven aging conditions, 40 condoms from each lot were randomly removed periodically (according to the experimental plan in Table II) and inflation-tested. The inflation test was performed as described in ISO 4074:2002 Annex G and in Ref. 17.

Data analysis

The data were analyzed statistically using STATISTICA.[13] Standard statistical analyses were performed, assuming that the experimental data were subject to random Gaussian fluctuations. It is important to emphasize that Gaussian fluctuations are usually assumed in most problems without any sort of experimental validation. In the present case, however, Figure 1 shows that assumption of Gaussian

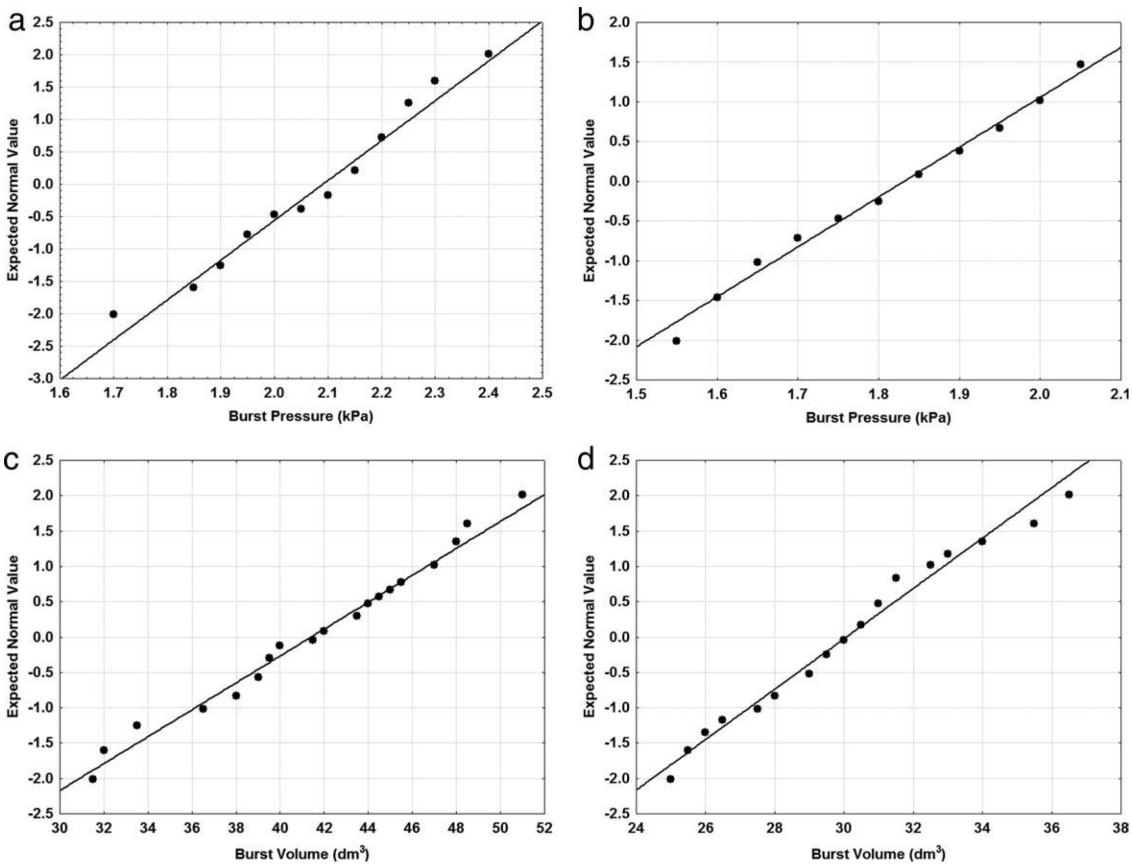

Figure 1 Illustrative example of the random Gaussian distribution of experimental data. Normal plots for burst pressure in lots (a) A3 51M, (b) E2 29M. Normal plots for burst volume in lots (c) A3 51M, (d) E2 29M. (M = months).

TABLE III
Proposed Models and Model Parameters for Pressure at Burst

Model 1	Model 2
Equation 3	Equation 4
$(P_0 - P_1) = t_i \exp\left[-\left(\frac{E}{R}\right)\left(\frac{1}{T_i} - \frac{1}{T_{ref}}\right) + A\right]$	$\left(\frac{P_1}{P_0}\right) = \exp\left\{-t_i \exp\left[-\left(\frac{E}{R}\right)\left(\frac{1}{T_i} - \frac{1}{T_{ref}}\right) + A\right]\right\}$

Note: Pi is the pressure (kPa) at time t_1; P_0 is the initial pressure (kPa) at time zero (no degradation); E is the activation energy (J mol^{-1}); R is the universal gas constant (= 8.314 J K^{-1} mol^{-1}); T_i is the experimental temperature (K); T_{ref} is a reference temperature (330K); A is a dimensionless constant.

For the individual lot models, P_0, E, and A are estimated, while for the aggregated models, E and A are estimated.

fluctuations of pressure and volume at burst is supported by independent experimental data.

Mathematical models

Two mathematical models were used. Both were based on the Arrhenius equation:

$$k(T) = \exp A \exp\left(-\frac{E}{RT}\right) \tag{1}$$

where k is the rate constant (or the specific reaction rate) for degradation, T is the absolute temperature, R is the ideal gas constant, A is a constant, and E is the activation energy. Both A and E are parameters of the Arrhenius equation.[18–21]

To minimize the high correlation between the parameters of the Arrhenius equation, eq. (1) was reparameterized.[10] When the Arrhenius equation is used without reparameterization, the confidence regions are curved (nonlinear) and the statistical interpretation of confidence regions may become meaningless. The use of a proper reference temperature and the reparameterization of the Arrhenius equation can improve the statistical interpretation of the confidence regions.[10–12] In this case, the Arrhenius equation must be written in the form:

$$k(T) = \exp\left(A - \frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \tag{2}$$

Model parameters were estimated with the least-squares technique. The estimation was based on average burst pressures and volumes available for the data sets for individual lots, according to the experimental design presented in Table II. Therefore, model parameters were estimated in the temperature range between 50 and 80°C and in the range of aging times between 2 and 182 days. A combination of the Hooke-and-Jeeves method and of the quasi-Newton method was used for optimization of the objective function, as already described. Models were tested for each individual lot and for the whole data set, containing all obtained experimental data for all products. Tables III and IV present the model equations and the respective model parameters. Model 1 [eqs. (3) and (5)] is a linear dynamic model (obtained when constant rate of degradation is assumed) and Model 2 [eqs. (4) and (6)] is a dynamic exponential model (obtained when a first-order rate of degradation is assumed).

RESULTS AND DISCUSSION

Modeling of burst pressure

Results obtained for Models 1 and 2 were very similar. Table V summarizes the parameters estimated for the pressure at burst, taking into account the individual lots (A1 to E2). Table VI shows the 95% confidence interval limits for the estimated model

TABLE IV
Proposed Models and Model Parameters for Volume at Burst

Model 1	Model 2
Equation 5	Equation 6
$(V_0 - V_1) = t_i \exp\left[-\left(\frac{E}{R}\right)\left(\frac{1}{T_i} - \frac{1}{T_{ref}}\right) + A\right]$	$\left(\frac{V_1}{V_0}\right) = \exp\left\{-t_i \exp\left[-\left(\frac{E}{R}\right)\left(\frac{1}{T_i} - \frac{1}{T_{ref}}\right) + A\right]\right\}$

Note: V_i is the volume (dm^3) at time t_1; V_0 is the initial volume (dm^3) at time zero (no degradation); E, R, T_i, T_{ref}, and A as defined on Table 3 (note).

TABLE V
Estimated Model Parameters for Pressure at Burst for Individual Lots

		Pressure (kPa)/Individual lots							
		Model 1				Model 2			
Lot	P_0^e	P_0^c	E (kJ mol^{-1})	A	R	P_0^c	E (kJ mol^{-1})	A	R
A1	2.15	2.05	121.82	−6.18	0.86	2.05	123.21	−6.87	0.87
A3	2.26	2.19	114.11	−5.89	0.89	2.20	115.30	−6.55	0.90
B2	2.29	2.21	121.10	−6.19	0.86	2.22	122.74	−6.89	0.87
B3	2.36	2.31	120.05	−5.82	0.91	2.32	121.89	−6.53	0.92
C1	2.51	2.43	138.82	−5.82	0.90	2.44	144.05	−6.59	0.91
C3	2.41	2.44	171.08	−6.77	0.92	2.44	178.77	−7.64	0.93
D1	2.39	2.42	−380.67	−23.14	0.50	2.42	1414.12	−39.27	0.31
D3	2.43	2.36	−27.88	−11.11	0.20	2.35	−29.08	−11.99	0.20
E1	2.00	1.99	109.52	−5.82	0.90	2.00	110.03	−6.38	0.91
E2	1.99	1.94	107.96	−5.48	0.98	1.96	110.64	−5.99	0.98

Note: P_0^e is the experimental value for P_0, P_0^c is the calculated value for P_0, E, and A were defined on Table 3 (note) and R is the correlation coefficient.

parameters P_0^c and E. From Tables V and VI, it can be observed that:

1. For each lot, the estimated parameters (P_0^c) obtained are very close to the experimental values (P_0^c).
2. For most products, R, the correlation coefficient ranges from 0.87 to 0.95, indicating satisfactory agreement between the models and experiments. Nonetheless, lots D1 and D3 behave differently—the pressure at burst increases as the temperature increases. As the structure of the proposed models assumes that the burst pressure decreases with temperature, agreement is not adequate in these cases. It is important to note that lots D1 and D3 were not packed in aluminum foil packages, but in plastic packages. This probably indicates that modification of the condom material was also affected by the atmospheric oxygen, as oxygen can permeate the thin plastic films that constitute the packages.
3. Estimated values for parameter E, the activation energy, range from 94 to 179 kJ mol^{-1}, which are in agreement with activation energies reported in the literature for degradation of natural rubber.[22] Lots D1 and D3 were the exceptions. These results were excluded from the analysis, as estimated E values were negative, which cannot be supported by physical reasoning.
4. Observed model deviations follow the normal distribution, as illustrated in Figure 2 and also observed for experimental data (see Fig. 1).

Figure 3 illustrates the quality of the model fit for burst pressure of lot E2. The horizontal bar represents the experimental error (ee = 0.048 kPa) calculated with 95% confidence from replicates. It can be observed that the model fit can be regarded as very good and that model deviations are comparable to the experimental error.

As most 95% confidence intervals for estimated model parameters P_0^c and E are statistically

TABLE VI
95% Confidence Limits (CL) for the Estimated Model Parameters for Pressure at Burst of Individual Lots

	Model 1				Model 2			
	P_0^c (kPa)		E (kJ mol^{-1})		P_0^c (kPa)		E (kJ mol^{-1})	
Lot	(−)CL	(+)CL	(−)CL	(+)CL	(−)CL	(+)CL	(−)CL	(+)CL
A1	1.99	2.11	91.87	145.94	1.83	2.28	41.34	199.22
A3	2.14	2.25	92.97	132.03	2.15	2.25	97.28	130.06
B2	2.13	2.29	84.88	152.29	–	–	–	–
B3	2.23	2.39	92.23	142.45	2.26	2.38	102.91	135.49
C1	2.37	2.49	118.58	160.13	2.36	2.51	113.99	175.78
C3	2.40	2.48	143.73	198.54	2.41	2.48	151.02	206.67
E1	1.88	2.08	66.31	155.34	1.90	2.08	75.99	146.60
E2	1.91	1.97	102.19	113.72	1.92	1.99	104.07	117.20

Note: (−) CL lower limit, (+) CL upper limit.

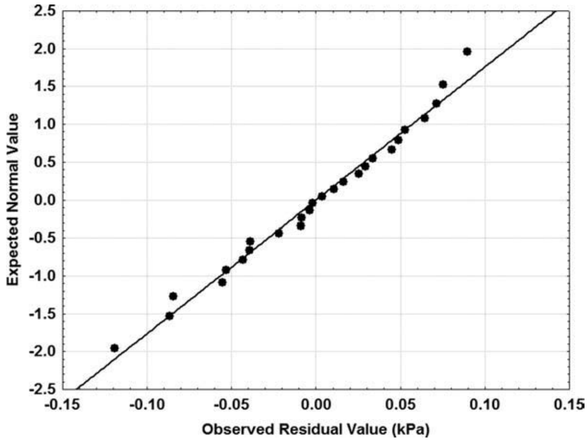

Figure 2 Normal *P* Plots for model residuals of burst pressure for lot E1 using Model 1.

equivalent, data obtained for samples produced by distinct manufacturers can probably be analyzed as a single set of experimental data. Nonetheless, it must be observed that the uncertainties for the activation energies are very high. Results on Table VI indicate that the activation energies of lots A3, B2, B3, E1 are probably different from activation energies of lots C3 and C1. (The confidence interval for lot E2 could not be obtained because of the very high correlation between the estimated model parameters.) Despite that, an attempt was made to represent all available data with a single set of model parameters. The experimental pressure drop ($\Delta P^e = P_0 - P_i$) was used as the response variable. The parameters E and A were estimated with eqs. (3) and (4) in Table III, respectively. Table VII presents the estimated model parameters (E, A), with the respective standard deviations (s_E, s_A), 95% confidence limits and the model correlation coefficient (R).

When the experimental data are analyzed as a single data set, standard deviations for both s_E and s_A decrease considerably, when compared with the individual lot analyses. This effect is related to the much larger degree of freedom of the second approach (individual lots contain 41 data values, while the whole experimental set contains 328 data values). On the other hand, the correlation coefficient decreases, showing that the quality of the model prediction becomes worse. Nonetheless, taking into account the intrinsic experimental variation of the burst pressure,[16] $R = 0.80$ can still be considered to be a reasonably good correlation coefficient. When outliers (experimental points whose model discrepancies cannot be explained by experimental fluctuations) were eliminated, the obtained activation energy was (111.72 $\pm$ 2.0) kJ mol^{-1}, while the correlation coefficient R increased to 0.84. Figure 4 illustrates the residual values ($\Delta P^e - \Delta P^c$) and shows clearly that residuals fluctuate symmetrically around zero, indicating once more the adequacy of the model.

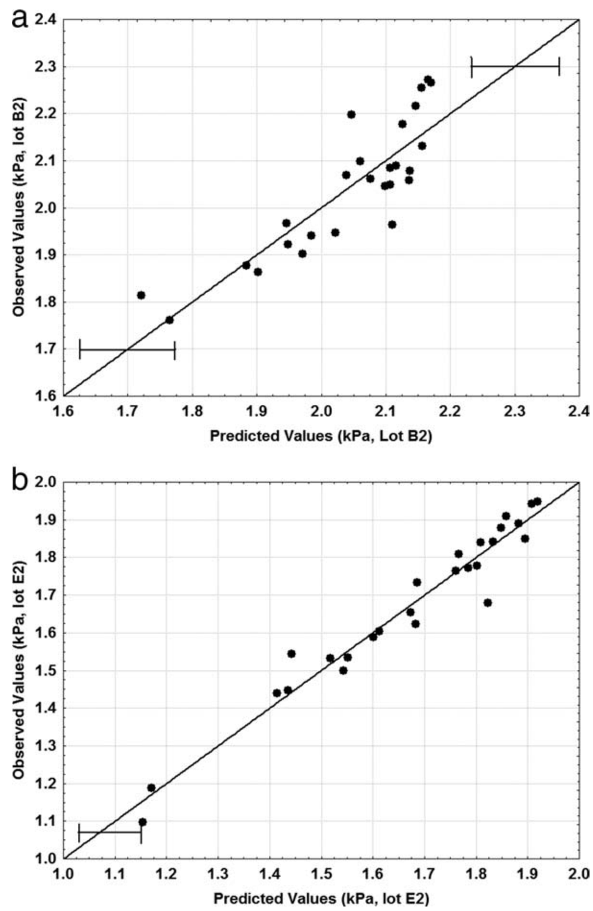

Figure 3 Experimental versus predicted values for P_i (kPa) using Model 1 for lots B2 and E2 in accelerated aging experiments (bar indicates the experimental error).

In summary, obtained results indicate that both Model 1 and Model 2 can be used to describe the degradation of pressure at burst of rubber male condoms at different storage conditions with good accuracy and sound statistical meaning. However, obtained results also indicate that the model

TABLE VII
Estimated Model Parameters for Pressure at Burst for all Data Values

	E (kJ mol^{-1})	s_E (kJ mol^{-1})	(−)CL$_E$ (kJ mol^{-1})	(+)CL$_E$ (kJ mol^{-1})	A	s_A	(−)CL$_A$	(+)CL$_A$	R
Model 1	112.66	2.28	108.19	117.14	−5.57	0.048	−5.67	−5.47	0.80
Model 2	114.32	2.96	108.53	120.12	−6.28	0.097	−6.47	−6.09	0.81

Note: (−) CL lower limit, (+) CL upper limit.

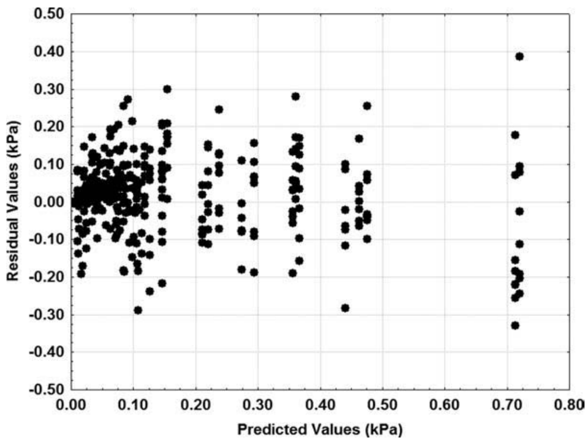

Figure 4 Model residuals (kPa) obtained for Model 1 using the whole set of burst pressure data.

parameters of different products can be different, indicating the different product performances at storage conditions. This explains why the model performance was prejudiced when the activation energies of the different materials were assumed to be the same, as usually proposed in the literature.[8,9] Therefore, it may be advisable that condom manufacturers perform accelerated aging experiments for proper characterization of the product performance.

Modeling of burst volume

The same methodology described previously was used for modeling of the degradation of burst volume. Table VIII presents the parameters estimated for the volume at burst, taking into account the individual lots (A1 to E2). Table IX presents the 95% confidence limits for estimated model parameters. In this case, Model 2 did not allow for good representation of volume at burst after estimation of model parameters. It can be observed that:

TABLE IX
95% Confidence Limits (CL) for the Estimated Model Parameters for Volume at Burst of Individual Lots

	V_0^c (dm^3)		E (kJ mol^{-1})		A	
Lot	(−)CL	(+)CL	(−)CL	(+)CL	(−)CL	(+)CL
A3	42.9	44.7	63.10	81.63	−3.79	−2.89
C3	36.4	39.2	53.02	75.36	−3.93	−2.63
D1	31.2	34.0	61.55	82.28	−3.62	−2.52
D3	32.7	35.9	53.19	77.30	−3.79	−2.41

Note: (−) CL lower limit, (+) CL upper limit.

1. For each individual lot, the estimated parameters (V_0^c) are always very close to the available experimental values (V_0^e).
2. The estimated activation energies, E, range from 51 to 72 kJ mol^{-1} and are much lower than the activation energies estimated for burst pressure. As both burst pressure degradation and burst volume degradation are consequences of latex modification, this may indicate that different factors control the degradation of burst pressure and burst volume. (Lot E1 was an exception, presenting an even lower activation energy, around 27 kJ mol^{-1}.) Estimated activation energies are smaller than usual values reported in the literature,[22] which seems to confirm that burst volume and burst pressure degradations may be controlled by different factors. Burst pressure can be related to latex resistance to rupture (resistance at break), while burst volume can be related to latex resistance to deformation (elasticity). Therefore, it can be said that latex elasticity is less sensitive to degradation than resistance at rupture.
3. Observed model deviations follow the normal distribution, as illustrated in Figure 5 and also observed for experimental data (see Fig. 1).

TABLE VIII
Estimated Model Parameters for Volume at Burst for Individual Lots

		Volume (dm^3)/Individual lots							
		Model 1				Model 2			
Lot	V_0^e	V_0^c	E (kJ mol^{-1})	A	R	V_0^c	E (kJ mol^{-1})	A	R
A1	37.7	38.7	69.53	−4.13	0.31	38.7	69.65	−7.67	0.31
A3	43.9	43.8	72.36	−3.34	0.65	43.8	72.24	−7.07	0.65
B2	38.1	35.6	68.05	−4.30	0.30	35.6	68.16	−7.85	0.30
B3	29.8	30.6	51.41	−4.92	0.42	30.6	51.02	−8.34	0.42
C1	39.6	37.5	62.59	−3.56	0.51	37.6	62.77	−7.12	0.51
C3	39.9	37.8	64.19	−3.28	0.65	37.8	63.90	−6.85	0.65
D1	34.0	32.6	71.92	−3.07	0.63	32.6	72.22	−6.47	0.63
D3	36.1	34.3	65.25	−3.10	0.66	34.4	65.30	−6.54	0.66
E1	31.0	29.8	27.27	−5.09	0.67	29.8	26.79	−8.44	0.67
E2	33.6	31.6	57.97	−3.54	0.75	31.7	57.27	−6.94	0.74

Note: V_0^e is the experimental value for V_0, V_0^c is the calculated value for V_0, E, and A were defined on Table 3 (note) and R is the correlation coefficient.

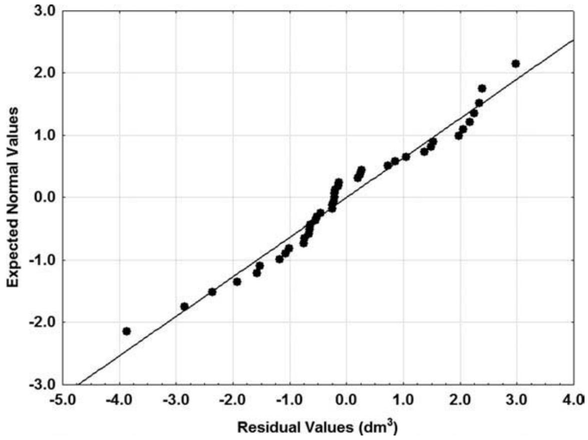

Figure 5 Normal *P* plots for model residuals of burst volume for lot E2 using Model 1.

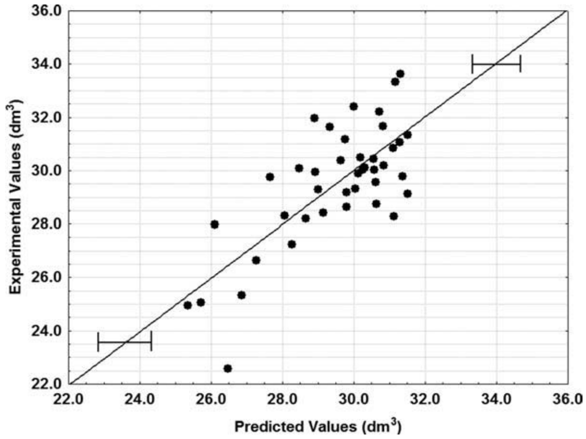

Figure 6 Experimental versus predicted values for V_i (dm^3) using Model 1 for lot E2 in accelerated aging experiments (bar indicates the experimental error).

Thus model deviations occur at random and follow the same statistical pattern observed for measured experimental data.

4. The obtained correlation coefficients, *R*, range from 0.30 to 0.75, indicating poor agreement with experimental data.

Figure 6 illustrates the quality of the model fit for burst volume of lot E2. The horizontal bar represents the experimental error (ee $=$ 1.96 dm^3) calculated with 95% of confidence from replicates. It is clear that the level of agreement for burst volume is not as good as for burst pressure. Despite that, available experimental burst volume data were grouped and analyzed simultaneously, as done previously with available burst pressure data. The experimental volume drop ($\Delta V^e = V_0 - V_i$) was used as the response variable. Parameters *E* and *A* were estimated using eq. (5) (Table IV) Table X presents the estimated parameters (*E*, *A*) with the respective standard deviations (s_E, s_A), the 95% confidence limits and the correlation coefficient (*R*). The correlation coefficients in this case are not good. Figure 7 illustrates the residual values ($\Delta V^e - \Delta V^c$) obtained for Model 1. Although residuals fluctuate around zero, fluctuations are asymmetric and indicate the existence of outliers. Nevertheless, identification and elimination of outliers does not lead to any significant improvement of the model fit and of the estimated model parameters. The performances of the burst volume models are improved when the individual lots are considered independently. Thus burst volume data obtained from different products and lots must be analyzed independently.

In summary, obtained results indicate that Model 1 (but not Model 2) can be used to describe the degradation of volume at burst of rubber male condoms at different storage conditions with good accuracy and sound statistical meaning. However, as in the case of pressure at burst, obtained results also indicate that the model parameters of different products can be different, indicating the different product performances at storage conditions. This explains once more why the model performance was prejudiced when the activation energies of the different materials were assumed to be the same, as usually proposed in the literature.[8,9] Therefore, as shown for pressure at burst, it may be advisable that condom manufacturers perform accelerated aging experiments for proper characterization of the product performance.

It is important to emphasize that the analysis of both pressure and volume at burst suggest that the degradation of rubber male condoms follows approximately constant degradation rate trajectories, although different products follow distinct degradation trajectories, requiring the independent characterization of the kinetic parameters.

TABLE X
Estimated Model Parameters for Volume at Burst for All Data Values

	E (kJ mol^{-1})	s_E (kJ mol^{-1})	(−)CL$_E$ (kJ mol^{-1})	(+)CL$_E$ (kJ mol^{-1})	A	s_A	(−)CL$_A$	(+)CL$_A$	R
Model 1	72.66	1.64	69.44	75.89	−2.843	0.052	−2.945	−2.741	0.43
Model 2	73.09	4.54	64.19	81.99	−6.737	0.204	−7.138	−6.337	0.24

Note: (−) CL lower limit, (+) CL upper limit.

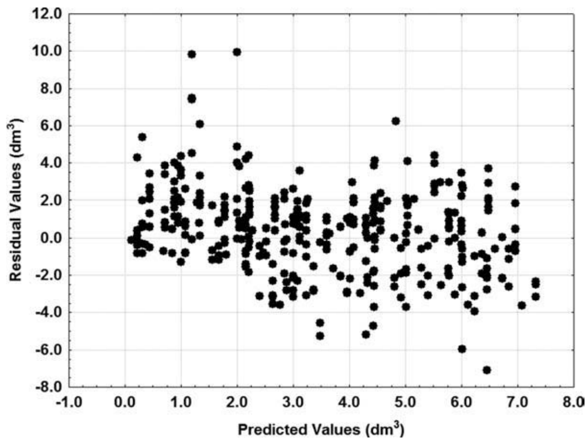

Figure 7 Model residuals (dm^3) obtained for Model 1 using the whole set of burst volume data.

Model validation

The validity of the proposed models was analyzed by evaluating their capacity to predict the measurements done in real time at 3 and 5 years. The results are shown in Tables XI and XII. The experimental results are shown with subscript *e* and the number of years, while the calculated (predicted) results are shown with subscript *c* and the number of years. In general, it is possible to observe that the predicted performances are in close agreement with the measured values for both burst pressure and burst volume. Observed differences are always lower than 10% for both values and are equal to 4% on average. (This indicates the usefulness of the proposed models, in spite of the low correlation coefficients obtained for burst volume, caused mostly by the large fluctuations of the experimental data.) These variations are also in agreement with the experimental repeatability for burst pressure and burst volume, as reported in proficiency trials of condom testing involving 86 distinct laboratories, where the repeatability for burst pressure and burst volume were found to be equal to 5.04% and 6.78%, respectively.[22,23]

Equations (3) and (5) (Model 1) can be used for prediction of shelf life only when initial test data are available. This is not a limiting factor because the quality control procedures require characterization of initial product performances at plant site. In this case, eqs. (3) and (5) can be rewritten in the form:

$$t_{\text{life}} = \frac{(P_0 - P_{\min})}{\exp\left[-\left(\frac{E}{R}\right)\left(\frac{1}{T_{\text{sto}}} - \frac{1}{T_{\text{ref}}}\right) + A\right]} \tag{7}$$

$$t_{\text{life}} = \frac{(V_0 - V_{\min})}{\exp\left[-\left(\frac{E}{R}\right)\left(\frac{1}{T_{\text{sto}}} - \frac{1}{T_{\text{ref}}}\right) + A\right]} \tag{8}$$

where t_{life} represents the shelf life of the product at the storage temperature T_{sto}. $P_{\min}$ and $V_{\min}$ are the minimum acceptable burst pressure and burst volume, as imposed by the norm.

Equations (3) and (5) [and eqs. (7) and (8)] also require the availability of the activation energies and pre-exponential factors, which are available only if accelerated aging experiments are carried out by condom manufacturers. Although this is not required by current quality control procedures, obtained results indicate that accelerated aging experiments should be performed at plant site for individual characterization of product performance, as different products present different performances at storage.

If individual kinetic parameters are not available, average parameters can be used for characterization of the product performance, as presented in Tables VII and X and illustrated in Figures 8 and 9. Figures 8 and 9 illustrate the predictive capacity of the proposed models when the average parameters presented in Tables VII and X are used for simulation. Dashed lines show the 95% confidence limits of the predicted values. As a whole, obtained results can

TABLE XI
Validation of Model Predictions for Burst Pressure

			Model 1				Model 2			
Lot	P_{3e}	P_{5e}	P_{3c}	(P_{3e}/P_{3c})%	P_{5c}	(P_{5e}/P_{5c})%	P_{3c}	(P_{3e}/P_{3c})%	P_{5c}	(P_{5e}/P_{5c})%
A1	2.06	2.06	2.02	101.7	2.01	102.6	2.02	101.8	2.01	102.7
A3	2.19	2.17	2.14	102.1	2.11	102.6	2.15	102.0	2.11	102.7
B2	2.21	2.32	2.18	101.2	2.17	107.1	2.19	100.9	2.17	106.8
B3	2.28	2.33	2.27	100.4	2.25	103.8	2.28	100.2	2.25	103.7
C1	2.42	2.58	2.41	100.4	2.40	107.6	2.42	100.0	2.41	107.2
C3	2.44	2.59	2.44	100.1	2.44	106.3	2.44	100.1	2.44	106.3
D1	2.34	2.27	2.30	101.8	2.22	102.3	2.42	96.7	2.42	93.8
D3	2.24	2.38	2.31	96.8	2.28	104.2	2.30	97.2	2.27	104.6
E1	1.89	1.84	1.93	97.8	1.89	97.1	1.93	97.8	1.89	97.4
E2	1.73	1.56	1.47	97.6	1.15	94.6	1.77	97.5	1.65	94.6

Note: P_{3e} and P_{5e} are experimental values for Pressure, with 3 and 5 years real time. P_{3c} and P_{5c} are predicted values, with 3 and 5 years, respectively.

TABLE XII
Validation of Model Predictions for Burst Volume

			Model 1				Model 2			
Lot	V_{3e}	V_{5e}	V_{3c}	$(V_{3e}/V_{3c})\%$	V_{5c}	$(V_{5e}/V_{5c})\%$	V_{3c}	$(V_{3e}/V_{3c})\%$	V_{5c}	$(V_{5e}/V_{5c})\%$
A1	38.6	36.7	37.4	103.3	36.5	100.6	37.1	103.9	36.1	101.5
A3	42.4	40.5	41.1	103.1	39.4	102.9	40.9	103.6	39.1	103.5
B2	37.4	33.1	34.4	108.7	33.6	98.5	34.3	108.9	33.5	98.7
B3	30.9	28.0	29.4	105.1	28.6	97.8	28.8	107.3	28.0	100.0
C1	33.5	32.1	34.4	97.3	32.4	99.1	34.3	97.6	32.3	99.4
C3	34.9	30.2	34.0	102.7	31.4	96.1	33.7	103.5	31.2	96.7
D1	27.8	25.9	29.1	95.7	26.7	97.0	28.8	96.5	26.5	97.7
D3	29.2	25.9	29.9	97.6	27.0	96.0	29.7	98.5	26.9	96.4
E1	28.4	26.8	27.3	103.9	25.7	104.2	27.2	104.2	25.7	104.4
E2	29.8	25.0	27.9	106.8	25.4	98.3	27.7	107.7	25.3	98.7

Note: V_{3e} and V_{5e} are experimental values for volume, with 3 and 5 years. V_{3c} and V_{5c} are predicted values, for 3 and 5 years, respectively.

be regarded as very good, as Lot D1 is the only one that lies outside the 95% confidence region range for the prediction of the degradation of pressure and Lot E1 for the prediction of the volume degradation.

CONCLUSIONS

Six brands of condoms were aged under subtropical ambient conditions for 5 years and under accelerated conditions at four temperatures for various times. The changes in burst pressure and burst volume were used as the indicators of product degradation. Experimental data were analyzed and two mathematical models (both based on the reparameterized form of the Arrhenius equation) were proposed. It was shown for the first time that it is possible to estimate and predict the degradation of natural rubber condoms with confidence with the help of the proposed models, based on data obtained from accelerated degradation experiments, provided that separate Arrhenius parameters are used for pressure and volume. The models were validated by comparing predicted results with those obtained experimentally after 3 and 5 years, and the results were within the reproducibilities found in interlaboratory trials. Using pooled data from all products, for degradation of burst pressure, the estimated activation energy was (112 ± 2) kJ mol^{-1}. For degradation of burst volume, the estimated activation energy was (74 ± 1) kJ mol^{-1}. The difference between the activation energies of the two properties indicates that the degradation of burst pressure and burst volume may be influenced by distinct factors during latex degradation. As the performances of the proposed models are improved when the individual lots are considered independently, individual manufacturers should be encouraged to estimate their own model parameters to improve the predictive performance of the shelf-life of their products.

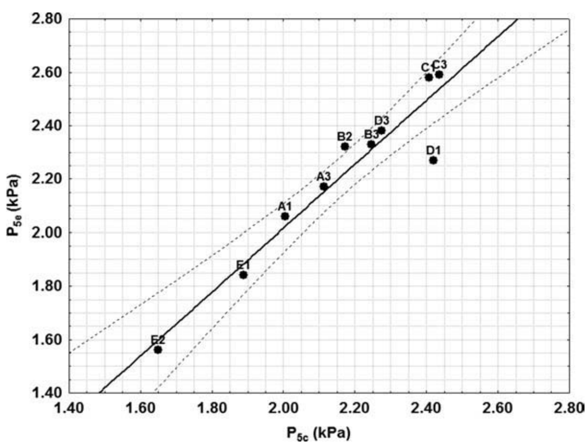

Figure 8 Validation of Model 1 for predicting the degradation of burst pressure. P_{5e} are the experimental values (kPa) after 5 years (real time) at 27°C and P_{5c} are the respective predicted values.

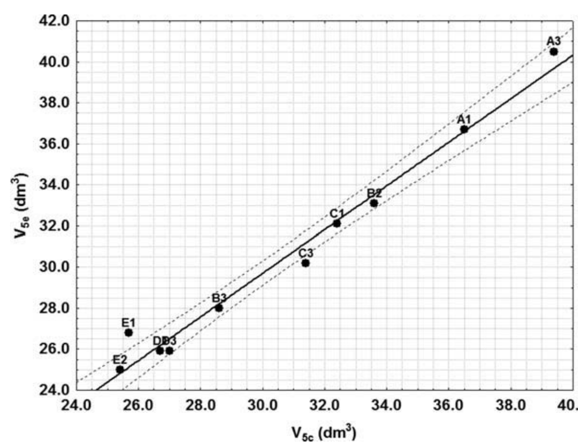

Figure 9 Validation of Model 1 for predicting the degradation of burst volume. V_{5e} are the experimental values (dm^3) after 5 years (real time) at 27°C and V_{5c} are the respective predicted values.

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