Mechanical Relaxations in Heat-Aged Polycarbonate. Part II: Statistical Analysis of Low-Molecular Weight Data

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The significance of heat-aging effects on low-molecular-weight polycarbonate has been studied by performing a two-factor Analysis of Variance (ANOVA). Although this work was primarily motivated by the large experimental scatter observed in stress relaxation results for LMW 2608 (Part I), the effect of heat-aging on the characteristics of secondary transitions (γ and β_1) generated by dynamic testing was also investigated. Both types of tests were performed using a dynamic mechanical analyzer. The statistical analysis verified an earlier suggestion that both the secondary transitions were insensitive to heat-aging. In the quasi-static stress relaxation tests, the curve-fitted KWW parameters (τ, E_o, β') were evaluated using ANOVA for increasing heat-aging time and test temperature. Two other statistical techniques were also applied to test repeatability—the *power* of each aging time/test temperature combination and the number of observations needed to achieve 90% repeatability. In conclusion, both τ and β' could describe the self-retarding nature of volume recovery although the repeatability of β' was substantially higher. However, the unrelaxed modulus, E_o, was found to be an unreliable indicator of whether heat-treatment had caused changes in the intrinsic structure. Overall, the study showed that the repeatability of the stress relaxation test results is generally very poor for the confidence levels tested.

INTRODUCTION

In Part I of this paper, a Dynamic Mechanical Analyzer (DMA) was utilized to determine secondary transitions (β_1, γ) in order to relate the relaxation of whole, or part of polycarbonate chain segments with the changes in stress relaxation behavior caused by progressive heat-aging. As expected, there was some experimental scatter in the generated relaxation curves and corresponding relaxation times acquired by testing a limited number of samples. Although the Kohlrausch-Williams-Watts (KWW) function pattern is commonly observed in polymers, it is generally accepted that the polymer relaxation phenomena can only be approximated by the stretched exponential function, which applies a single decay rate. A distribution function to represent the broad range of relaxation times (e.g. 1, 2) is considered more accurate because of the large variation in possible modes of dynamic motions along the chain. Various complex dynamic models (e.g. 3) that would account for the fluctuations or random nature of local molecular motions have been proposed in the literature.

The small sample size used in Part I also contributed to the experimental scatter. Typically, when generating data either for research or quality control, one or two data sets are usually considered sufficient to qualitatively compare or describe cause-effect relationships. This is due to time and cost constraints, which make it not feasible to fully characterize stress relaxation response by conducting large number of tests. Moreover, little is known about the repeatability of such tests.

Stress relaxation results in Part I showed that in some sets of data for low-molecular-weight Makrolon 2608 polycarbonate (LMW-PC), the variation between data points appeared only slightly greater than the extent of scatter. As compared to high-molecular-weight Makrolon 3208 polycarbonate (HMW-PC), the effects of heat-aging were harder to discern. Given that the numerical findings for LMW-PC data were close in value, particularly with overlapping standard deviations, a

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formal test procedure should be conducted to detect objective trends within each set of results, and between two or more sets of results. In this work, we performed a separate set of dynamic scans and stress relaxation tests on LMW-PC. The purpose was to apply two-factor Analysis of Variance (ANOVA) models to test the significance of main effects, i.e. heat-aging and test temperature, and two-way interactions. Analysis was performed using a commercial statistics package known as Minitab®, Version 13.

APPLICATION OF ANOVA ANALYSIS

Analysis of Variance, abbreviated ANOVA, is a broad term used to describe 'a collection of experimental situations and statistical procedures for the analysis of quantitative responses from experimental units' (4). Experimental units may refer to treatment or population means. The characteristic that differentiates between the treatments or populations is called the *factor* under study, and the *levels* of the factors differentiate characteristics within the treatments or populations. For a two-factor ANOVA, factor A will have I total number of levels i, and factor B will have J total number of levels j, thus creating IJ possible combinations consisting of one level of factor A and one of factor B. Individual combinations of factors and levels are referred to as a treatment, so there are IJ different treatments. For example, the dynamic scans performed in this work has factors A: (heat-aging time at 120°C), B: (frequency), and the levels are i_{1-10}: (0, 1, 3, 5, 7, 9, 24, 48, 96, 120 hours), j_{1-2}: (0.1, 1 Hz), and the total number of treatments is IJ: 20. For the stress relaxation experiments, the factors are A: (heat-aging time at 120°C), B: (stress relaxation test temperature), and the levels are i_{1-5}: (0, 24, 48, 96, 120 hours), j_{1-4}: (50, 80, 100, 120°C) and the total number of treatments is IJ: 20. A third variable, K, can be used to account for the number of observations performed within each treatment. The number of observations made on treatment (i,j) will be denoted as K_{ij}. In this work, K_{ij} was chosen to be 2 for the dynamic scans and 5 for the stress relaxation tests, for a total number of tests IJK: 40 and IJK: 100, respectively. Although ANOVA may be performed on data where K_{ij} is only 1, $K_{ij} > 1$ will allow the repeatability of results to be evaluated with further statistical calculations beyond ANOVA.

Experimental Design

Designing experiments to follow a two-factor ANOVA lends to objective testing on whether or not the factors of heat-aging time, frequency and test temperature are affecting the material's response when tested by dynamic spectra or stress relaxation experiment. The test is written in the form of a null hypothesis, H_0, and an alternative hypothesis, H_a, where

H_0: there is no effect

H_a: there is an effect

For example, there may be one effect (A), a second effect (B), and an interaction (AB) between the two factors. An interaction occurs if the difference in true average responses for different levels of one factor depends on the level of the other factor (4). The two-factor ANOVA test procedure is based on comparing a measure of differences between-sample variation to a measure of variation calculated from within each of the samples. A sample refers to the data grouped by a single level within one factor, whereby the levels of the other factor are ignored. To evaluate the independence of levels within and between factors, a model such as in *Eq 1* is established:

$$X_{ijk} = \mu + \alpha_i + \beta_j + \gamma_{ij} + \epsilon_{ijk} \quad (1)$$

where X_{ijk} is the random variable when factor A is at level i and factor B is at level j,

μ is the expected response averaged over all levels of both factors (the true grand mean),

$\alpha_i = \mu_{i\bullet} - \mu$ = the main effect of factor A at level i,

$\beta_j = \mu_{j\bullet} - \mu$ = the main effect of factor B at level j,

$\gamma_{ij} = \mu_{ij} - (\mu + \alpha_i + \beta_j)$ = the interaction parameter,

ϵ_{ij} = the random amount by which the observed value differs from its expectation and the ϵ_{ij}'s are assumed normal and independent with common variance σ^2, and

$\mu_{i\bullet}$ = the expected response averaged over all levels of the second factor when the first factor A is held at level i, and similarly for $\mu_{j\bullet}$.

Essentially, α_i, β_j and γ_{ij} are differences in means, whereby a difference not equal to zero at a given level suggests that there is an effect. Accordingly, there are three hypotheses to consider:

H_{0AB}: $\gamma_{ij} = 0$ for all i, j versus
H_{aAB}: at least one $\gamma_{ij} \neq 0$

H_{0A}: $\alpha_1 = \ldots = \alpha_I = 0$ for all i, j versus
H_{aA}: at least one $\alpha_i \neq 0$

H_{0B}: $\beta_1 = \ldots = \beta_J = 0$ for all i, j versus
H_{aB}: at least one $\beta_j \neq 0$

If H_0 is true for factor A, then I observations in each sample come from a normal population distribution with the same mean value μ, in which case the sample means within each treatment with respect to only the factor A, should be reasonably close, i.e.

$$X_{i\bullet k} = [\Sigma^{1}_{i=1} \Sigma^{K}_{k=1}(Xij)]/(IK) \quad (2)$$

If the sample means are not close, then the H_0 is rejected, and the H_a describes the true state of nature.

The ANOVA user must be made wary of interaction. If H_{0AB} is not rejected, then the other two hypotheses can be tested to see whether the main effects are significant. If H_{0AB} is rejected, the model does not lend

itself to straightforward interpretation and the reason why the factors interact should be sought.

Treatment of Data

There are some assumptions implied in ANOVA tests. First, the number of data points within each (i,j) treatment are the same, i.e. K is consistent. An unbalanced number of data points in any treatment will require a review and selection of other statistical analysis approaches. Second, the samples are randomly selected or tested from a population. Third, the I and J population or treatment distributions are all normal with the same variance σ^2. That is, each X_{ij} is normally distributed with

$$E(X_{ij}) = \mu_{ij};\ V(X_{ij}) = \sigma^2 \quad (3)$$

where X_{ij} is a random variable denoting the measurement when factor A is held at level i and factor B is held at level j, $E(X_{ij})$ represents the average of all the observations within treatment (i,j), μ_{ij} represents the normally distributed mean, $V(X_{ij})$ represents the variance of all the observations within treatment (i,j), and σ^2 represents the normally distributed variance. When the variances between treatments (i,j) are all the same (or reasonably so), the data is considered homoscedastic. In the case where the variances have significant discrepancies between them, the data is called heteroscedastic. Heteroscedasticity is a serious problem and could mean that the data outliers that are causing some variances to be significantly large compared to the others are affecting the observed trends. The removal of data outliers makes sense when it can be proven that the outliers resulted from error in recording data values or experimental errors. If there is no assignable cause, the statistical model should be reported with and without the outliers. However, extracting outliers from a set of data would make the ANOVA design unbalanced, and hence not computationally possible. In the case of extreme data outliers, other statistical models should be reviewed. In this work, data outliers were not removed, but heteroscedasticity was taken into consideration.

One method of reducing or eliminating heteroscedasticity is to *transform* the raw data. Some commonly used transformations include $(X_{ijk})^{1/2}$, $(X_{ijk})^{1/3}$, $(X_{ijk}{}^{1/3} - 1)/3$, $\log(X_{ijk})$, and $\log(\log(X_{ijk}))$. Transformations reduce the magnitude of the data, and hence reduce the magnitude of the variability, as well as the significance of the variability in the case of logarithmic transformations.

TESTS FOR REPEATABILITY

We also performed two additional statistical calculations, apart from ANOVA, to evaluate the repeatability of experiments performed. The first calculation was *power*. The power of an experiment predicts the probability that the same experiment performed in the future will not result exactly in the same mean value, but alternatively will deviate from the mean by a specified amount. For this work, the current mean value was compared to a fictitious future mean value, which differed by 10%. After determining the power of the experiment relative to the amount of test replicas used, a second calculation was performed to find the number of observations, N, required to achieve a minimum power of 0.80 (or 80% probability).

EXPERIMENTAL

Sample Preparation and DMA Instrument

Makrolon® 2608 is an unmodified, low-molecular-weight, bisphenol-A polycarbonate produced by the Bayer Corporation, Pittsburgh. Injection molded rectangular bars were received from the Polymers Division at Bayer. Molding was conducted at 138 MPa (20,000 psi) injection pressure and 83 MPa (17,000 psi) hold pressure, and subjected to normal in-mold cooling conditions with a cycle time of approximately 40 seconds. The dimensions of each bar were: length 152.5 mm, width 12.88 ± 0.03 mm, thickness 3.15 ± 0.007 mm. The samples were stored in sealed plastic bags in a desiccator. Heat-aging was performed at 120°C in a hot air circulating oven. The selected heat-aging temperature was based on previous results (5) for high-molecular-weight Makrolon® 3208 which showed a significant reduction in impact resistance when heat-aged at 120°C.

Dynamic mechanical scans and stress relaxation tests were performed on the TA Instruments Dynamic Mechanical Analyzer (DMA) 2980 Model. The molded bars were cut in two and the ends trimmed with a dry rotating blade to allow for sufficient overhang (as specified by ASTM D790) at both ends of a 50 mm span three-point bend clamp. Each sample was loaded in the clamp following the procedures described in (6) and displaced at the center by the drive shaft. In the DMA 2980, the applied static and dynamic forces are measured as separate entities.

Dynamic Mechanical Scans

Dynamic scans were performed on unaged and samples aged for 1, 3, 5, 7, 9, 24, 48, 96 and 120 hours. After loading in the DMA, each sample was rapidly cooled to −130°C using liquid nitrogen and then heated at a rate of 2°C/min to 160°C. A 100 μm displacement amplitude was applied and tests were performed at two different frequencies, 0.1 and 1 Hz. The DMA scans were generated in terms of loss tangent, tan δ, measurements as a function of temperature, similar to *Fig. 2b* in Part I of this paper.

As stated earlier, there were 20 different treatments (IJ) due to the combinations of frequencies and aging times, and two test replicas (K) for each treatment for a total of 40 tests (IJK). The sequence of testing for each set was randomized using a Design of Experiments (7) approach, which followed a complete block two-factor factorial method.

A relatively small static force of 1 N was used to maintain contact between the specimen and drive shaft at the beginning of the experiment. However,

this pre-tension static force is automatically adjusted throughout the experiment because the test was conducted using an 150% autostrain condition (8). Autostrain is a constant multiplier used to adjust the static force as the material being oscillated changes its stiffness. The static force is adjusted according to the following expression (8):

$$\text{Static force} = \text{autostrain x sample stiffness x oscillation amplitude} \quad (4)$$

This allows the oscillating force to increase if the force in the sample is reduced, thereby ensuring that the sample is securely held by the drive clamp and there is no play. Conversely, the force will decrease to prevent buckling if the sample is under excessive load.

Stress Relaxation Testing

Stress relaxation tests were performed on the same batch of injection molded samples as in Part I of this paper but heat-aged at two different time periods. The first set (Set 1) was heat-aged within a month of injection molding. The preliminary work was aimed at comparing unaged with 24-hour aging since it was observed in Part I that the effects of heat-aging were immediate but difficult to evaluate because of wildly scattered data points. In this set, the stress relaxation tests were performed at 50, 80, 100 and 120°C. Five individual tests were conducted for each combination giving a total of 80 tests.

In the second set (Set 2) of tests, performed seven months later, heat-aging was performed for 48, 96 and 120 hours. As in the first set, DMA scans were done at 50, 80, 100 and 120°C on five test replicas for each condition. The number of treatments was 20 (IJ) and the number of test replicas was 5 (K), giving a total number of 100 (IJK). Given that the physical aging process is very slow, the seven-month interval was not expected to affect results. However, since the DMA 2980 instrument was recalibrated during that period, which could subtly affect the results, the two data sets were analyzed separately. The test sequence for each set was randomized using a Design of Experiments (7) approach of a complete block two-factor factorial method.

A single-step strain of 0.05% was applied (roughly 100 μm at ambient temperature) in each stress relaxation experiment. Neither a pre-tension static force nor the autostrain option was necessary. In the three-point bend type test, the force and displacement are used to compute the modulus as it changed with time at each isotherm (8):

$$E = K_s L^3/6I\,[1 + 12/5(1 + \upsilon)(t/L)^2] \quad (5)$$

where E is the elastic modulus for the rectangular sample, L the sample length, t the sample thickness, I the sample moment of inertia, υ the Poisson's ratio, and K the measured stiffness which incorporates the changes in applied force with time. The sample stiffness is defined as the force applied to the sample divided by the amplitude of deformation (8).

STATISTICAL MODEL

Following *Eq 1*, the statistical model for evaluating dynamic scan data is as follows:

X_{ijk} = secondary relaxation temperature, or tan δ

= μ: (grand mean) + α_i: (aging time effect) + β_j: (frequency effect) + γ_{ij}: (interaction between aging time and frequency) + ϵ_{ijk}: (random error)

where X_{ijk} represents the measured raw data in units of °C or is unitless.

The hypotheses tested are expressed as:

H_{01}: there is no aging time effect versus
H_{a1}: there is an aging time effect

H_{02}: there is no frequency effect versus
H_{a2}: there is a frequency effect

H_{03}: there is no interaction versus
H_{a3}: there is an interaction

The expression for modeling experimental KWW material functions obtained from stress relaxation experiments is:

X_{ijk} = KWW equation parameters, τ, E_o or β′

= μ: (grand mean) + α_i: (aging time) + β_j: (test temperature) + γ_{ij}: (interaction between aging time and test temperature) + ϵ_{ijk}: (random error)

where X_{ijk} represents the measured raw data in units of minutes, MPa or is unitless.

The hypotheses tested are expressed as:

H_{04}: there is no aging time effect versus
H_{a4}: there is an aging time effect

H_{05}: there is no test temperature effect versus
H_{a5}: there is a test temperature effect

H_{06}: there is no interaction versus
H_{a6}: there is an interaction

Both models were tested using the a commercial statistics package known as Minitab®, Version 13. It was decided *a priori* that the experimental results would be evaluated at a minimum level of significance $\alpha = 0.10$, or 90%, to reject the null hypothesis. The level of significance, α, is compared to P-values calculated by the statistics package for each factor and interaction. If the P-value is above the level of significance, the H_0 is not rejected. If the P-value is below the level of significance, the H_0 is rejected and the H_a is said to describe the true state of nature. For example, if Minitab® calculates a P-value of 0.200 for the aging time factor, this means we are 20% confident that H_0 describes the true state of nature, or 80% confident that H_a describes the true state of nature. Since our α-level chosen to determine whether the effect is significant is

0.10, the H_0 is not rejected and the statement can be made that there is no significant aging time effect. The opposite conclusion would be true if the P-value were 0.000; i.e. the H_0 would be rejected stating that aging time has a significant effect on the material's response. It is customary to state the data as significant when H_0 is rejected and not significant otherwise (4). Simply,

(i) $$P\text{-value} \leq \alpha \Rightarrow \text{reject } H_0 \text{ at level } \alpha \quad (6)$$

(ii) $$P\text{-value} > \alpha \Rightarrow \text{do not reject } H_0 \text{ at level } \alpha \quad (7)$$

Minitab® also provides the user with plots of residuals, denoted by e, versus fitted/predicted values. The plots are examined to confirm the choice of model (i.e. two-factor ANOVA) or for indications that the model is not appropriate. *Figure 1* illustrates several plots that indicate abnormality in data, or heteroscedasticity. In general, a plot such as *Fig. 1* should have an elliptical shape around zero on the Y-axis, meaning that the data has a normal distribution, or is homoscedastic.

Testing for Repeatability

There are two possible errors when performing hypothesis testing. The first error arises when H_0 is rejected although it is true, i.e. a Type-I error. The second error is when H_0 will not be rejected when the H_a rightly represents the true state of nature or a Type II error (4). This decision process is illustrated in *Table 1* (9). The ANOVA test decides whether or not to reject H_0, and hence the P-value is the (conditional) probability (α) that we have just made a mistake, a Type I error (9). A Type II error, however, is not accounted for by the ANOVA test. As a result, the *power* test is used to determine the probability (θ) that our decision not to reject H_0 will result in a Type II error. A power test is applied in conjunction with the ANOVA test, using the mean and standard deviations for each individual treatment from the experimental results and a specified H_a. It is, however, noted that the power test is not rejecting an H_0 on the basis of a P-value, which is an ANOVA test procedure. The power test has *a priori* set H_a to a value and is testing how reliable the decision is to reject H_0 and accept H_a—a Type II error. The power of an experiment predicts the probability ($1 - \theta$) (9) that the same experiment performed in the future will not result exactly in the same mean value, but alternatively will deviate from the mean by a specified amount, H_a. Hence, a low power value means that the probability a Type II error is made is high. For this work, the current mean

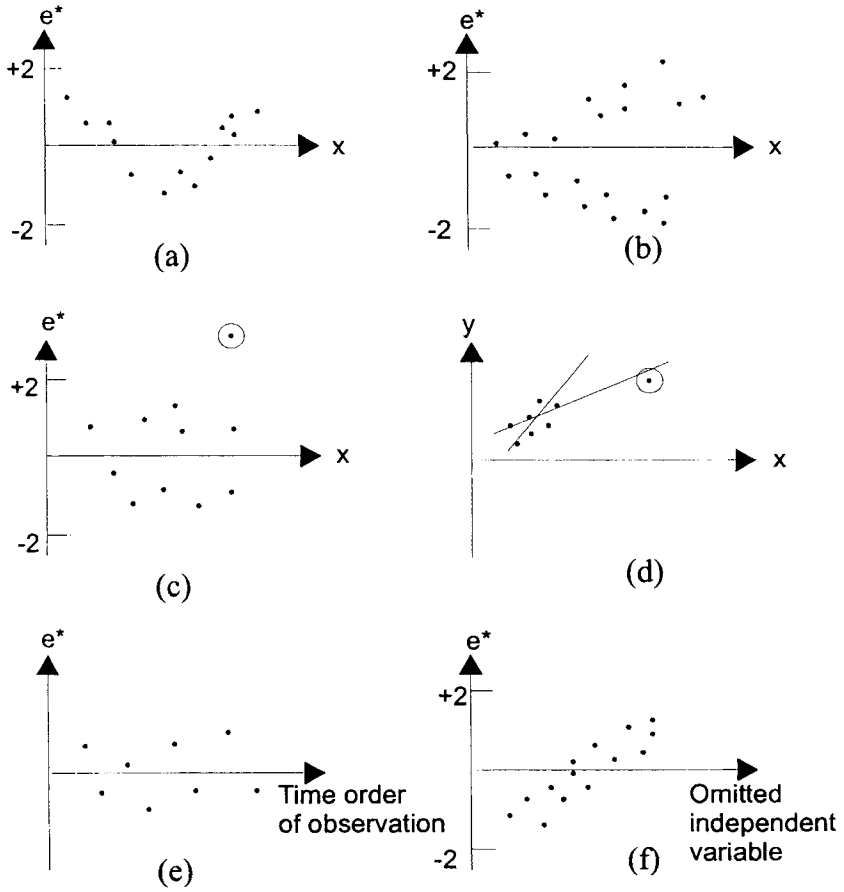


Fig. 1. Plots that indicate abnormality in data: (a) nonlinear relationship; (b) nonconstant variance; (c) discrepant observation; (d) observations with large influence; (e) dependence in errors; and (f) variable omitted.

Table 1. Hypothesis Decision Errors.

Decision	True State of Nature: H_0	True State of Nature: H_a
Fail to reject H_0	Correct decision ($1 - \alpha$)	Type II error (θ)
Reject H_0	Type I error (α)	Correct decision ($1 - \theta$)
	1	1

value for individual treatments was compared to a fictitious mean value (the future mean value) that differs by 10%. *Current* refers to the present experimental data. Hence, the hypothesis for the power test is:

H_{07}: a future test mean = the mean value of the current experiment data

H_{a7}: a future test mean = 1.10 × (the mean value of the current experiment data)

With this hypothesis in mind, power is therefore the probability that H_{a7} correctly describes the state of nature if we reject H_{07}. A power of 0.80, or probability of 80%, is deemed acceptable in this work, although it may not be appropriate in all circumstances. If the power is higher than 0.80, it is reasonable to suggest that future test results will lie within 10% of the current mean. However, if the power is lower than 0.80, a future test result will likely be beyond the 10% difference, and our repeatability of results for this type of experimentation is deemed poor by this work's standard. A confidence level of 95% ($\alpha = 0.05$) has been used in the power calculations.

The final calculation performed in this work was to find the number of test replicas/observations, N, required to achieve a nominal power of 0.80. Again, a confidence level of 95% ($\alpha = 0.05$) was used, and the mean and standard deviations from the experimental data collected. Sample calculations for both power and the number of observations are shown in the **Appendix**.

RESULTS AND DISCUSSION

Dynamic Mechanical Spectra

Figures 2a and *b* illustrate the temperatures and associated tan δ values for secondary transition peaks γ and β_1. The ANOVA *P*-value analyses are given in *Table 2*. The high *P*-values reveal that there is no aging time effect on the γ and β_1 secondary relaxation transitions, nor are there any interactions. Test frequency appears to affect the temperature of the γ peak but not its tan δ magnitude. The converse is true in the case of the β_1 transition. Since there is no aging time effect, the average values for all the experiments for the two frequencies were calculated and shown in *Table 3*. It is interesting that the first data set (D1) for the γ transition temperature, T_γ, has higher variability than D2. Also in *Table 3*, as the frequency is increased, the values of peak temperature and tan δ increase. An increase in tan δ suggests decreasing elastic stiffness.

Stress Relaxation Tests

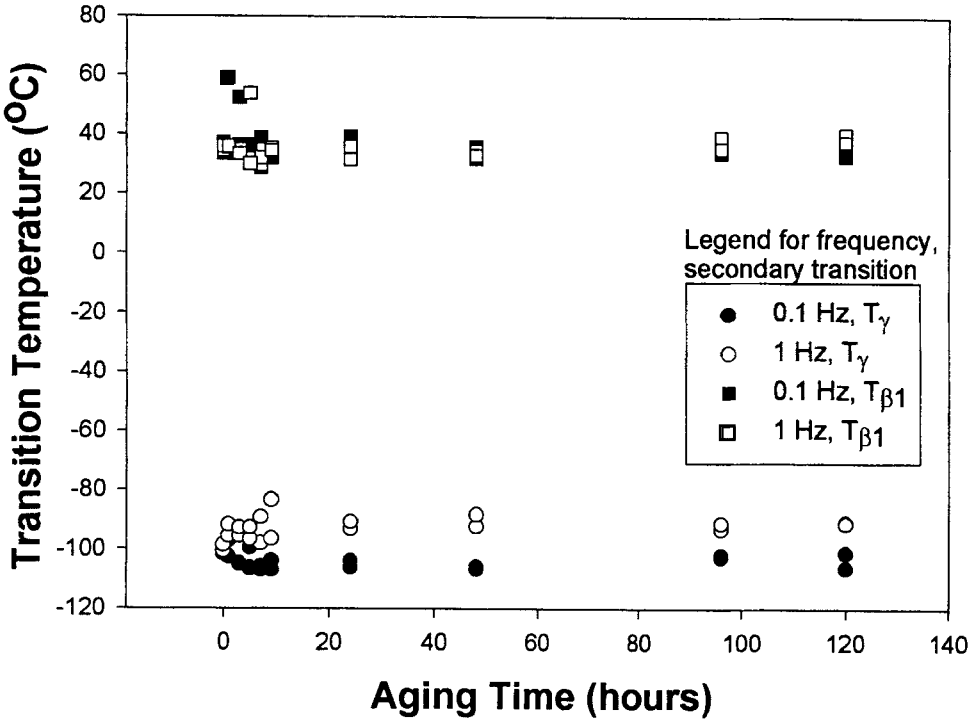
In Part I, we showed how the the stretched exponential expression by Kohlrausch-Williams-Watts can be applied to characterize stress relaxation behavior. The KWW parameters E_o, τ and β′ have been determined by curve fitting each stress relaxation curve using SigmaPlot® Ver.4 software. The reader is reminded here that Sets 1 and 2 were tested in the same DMA instrument but about seven months apart. For each parameter, the values have been plotted against aging time and test temperature, with standard deviations denoted by error bars in *Figs. 3* to *6*. In each case, the ANOVA test results performed using Minitab® are provided and discussed.

Effects on Relaxation Time Constant, τ

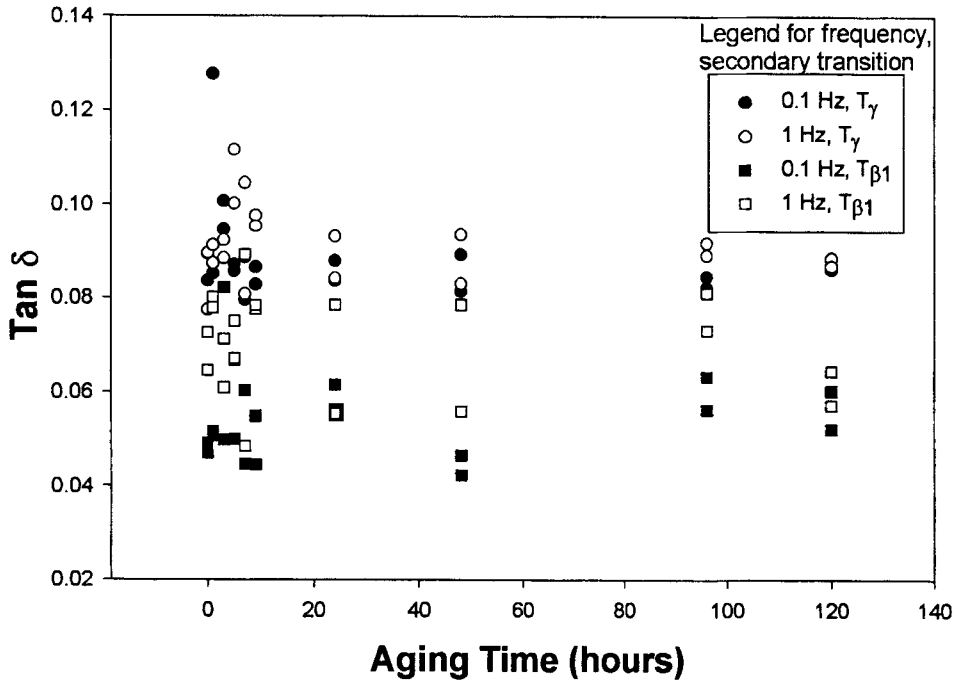
In *Fig. 3a*, the relaxation time increases with heat-aging time up to either 24 or 48 hours, and then begins to level off. However, it is possible to continuously initiate relaxation in LMW 2608 polycarbonate even after prolonged heat-aging, as long as the test temperature is high, e.g. at 120°C, *Fig. 3b*. At lower temperatures, e.g. 50°C and 80°C, much of the relaxation processes occur within the first 24 hours of heat-aging. Even at 100°C, the DMA was not able to detect any change in structural relaxation after 48 hours of heat-aging.

In *Fig. 3b*, the relaxation time generally decreases with increasing temperature, which is expected. In the unaged state, the higher the temperature, the faster the relaxation. In the aged conditions, however, the relationship is not as simple. After 24 hours of aging, molecular relaxation becomes severely suppressed, and this does not change until the temperature is increased to at least 80°C. For even longer aging up to 120 hours, molecular mobility was delayed further until 100°C.

Table 4 shows the mean values and standard deviation of the relaxation times. There is large variability between the five replicas for some of the conditions. Since the level of variability between the two data sets was quite significant, it was necessary to use a log (log(τ)) transformation on Set 1 (0, 24 hours aged), and a log(τ) transformation on the Set 2 (48, 96, 120 hours aged) to reduce the heteroscedasticity. Otherwise, it would not have been possible to perform an accurate ANOVA test on the raw data because ANOVA assumes the data is homoscedastic. After transformation of the two sets, the heteroscedasticity was reduced significantly, which was observable by plotting the residual versus fitted values. The *P*-values were determined and are shown in *Table 5*.



(a)



(b)

Fig. 2. The effects of heat-aging on transition temperature and tan δ magnitude of the β_1 and γ relaxations for two sample sets.

Table 2. *P*-values for Secondary Relaxation Transitions Based on ANOVA Tests.

Effect	T_γ (°C)	T_γ tan δ	$T_{\beta 1}$ (°C)	$T_{\beta 1}$ tan δ
Aging Time	0.879	0.46	0.7	0.847
Frequency	0	0.363	0.562	0
Interaction	0.184	0.279	0.714	0.672

The *P*-values for Set 1 (0, 24-hour heat-aged) indicate that there are significant aging time and test temperature effects and an interaction between the two effects. In unaged samples and aged up to 24 hours, it is seen that heat-aging retards relaxation and that increasing test temperature decreases relaxation times. In Set 2, *P*-values reveal that there is only a test temperature effect. Therefore, the aging time/test temperature interaction observed in Set 1 clearly demonstrates the immediate effects of heat-aging on structural change, i.e. the impact is observed within the first 24 hours. Beyond that, heat-aging effects tend to diminish. This finding is consistent with the self-retarding nature of structural change in the form of free volume contraction with increased aging time (10). Given that the heat-aged polycarbonate chains remained inflexible in most part, *Fig. 3b*, the temperature effect found (*P*-value = 0.00) in Set 2 is most likely a manifestation of the drastic decrease in relaxation time at test temperatures above 120°C.

Although the significance of the trends are made very clear by the ANOVA tests, it is important for future work to evaluate the repeatability of these results because there is large variability, as noted in *Table 4*. Since the data is so heteroscedastic, 95% confidence intervals should be calculated based on the means and standard deviations of each test condition, rather than using the Mean Standard Error (MSE) derived from the ANOVA test, which combines the effects of every condition within the respective sets. The calculated power of each test is listed in *Table 6*. The number of tests, N, required to achieve a power of 0.8 is also included. It is seen that not only is the probability of future test results existing within 10% of the current mean is extremely low, i.e. power values are low, but the number of tests required to reach a power of 0.80 (or 80% probability) is not practically attainable for most conditions. In fact, the test with the highest probability of repeatability—unaged state at 100°C—will require at least 32 tests to achieve 80% probability of achieving values within 10%.

Effects on Unrelaxed Modulus, E_o

We pointed out in Part I of this paper that the E_o values obtained from KWW curve fitting were, in some cases, quite different from the values read off from the raw stress relaxation curves. Accordingly, we performed a statistical analysis on the KWW unrelaxed modulus, E_o, as well as the experimental value, E_{raw}.

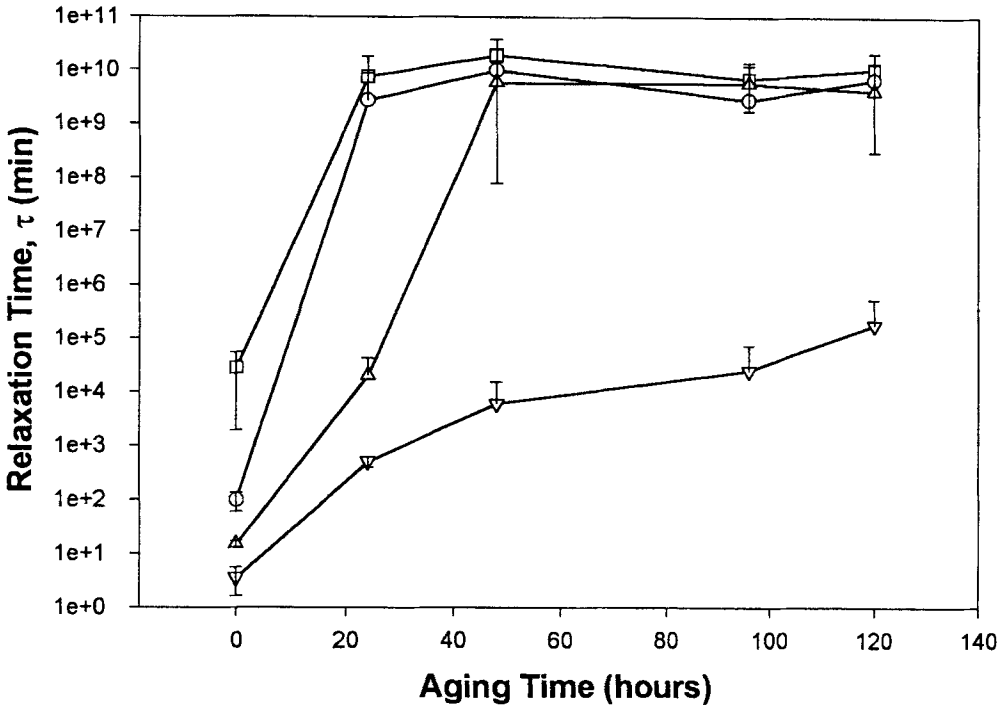
As shown in *Fig. 4* for E_o, it is unclear if heat-aging time or test temperature affects the unrelaxed modulus. In the raw test data shown in *Fig. 5*, however, there is only a hint of test temperature effect. When analyzed statistically, the variability in both cases, although high, appeared to be relatively consistent for all conditions and hence transformations of the raw data did not change the ANOVA results significantly. In *Table 7*, the *P*-values for E_o indicate that a test temperature effect is evident but there is no heat-aging time effect or interaction. This is seen in Set 1, *Fig. 4b*, where E_o values slightly decrease with increased test temperature. The temperature effect detected in Set 2 results is described by a higher *P*-value. From *Figs. 4a* and *b*, the difference in *P*-value is most likely caused by an increase in unrelaxed modulus at 100°C, which is not observed in the other second set test conditions.

When E_{raw} was analyzed, an aging time effect, test temperature effect and interaction were very evident for Set 1. In Set 2, only a test temperature effect was observed. It appears then that E_{raw}, but not E_o, tends to reflect the similar effects found earlier in τ.

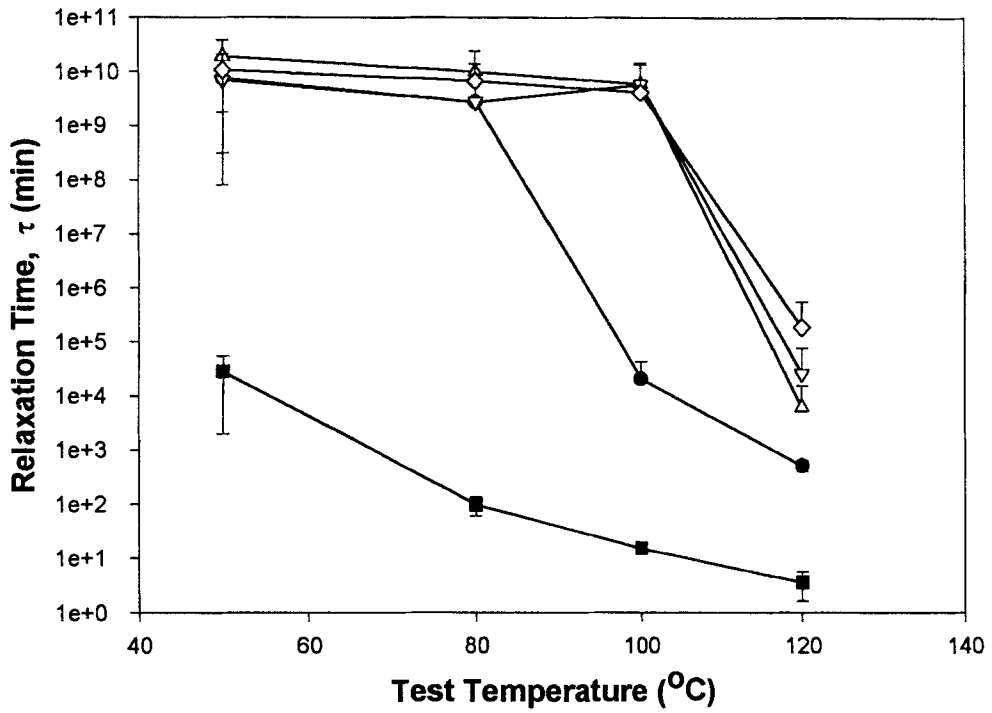
Consistent with observations in Part I, there is a strong suggestion that the KWW unrelaxed modulus cannot be a reliable indicator of structural changes caused by heat-aging or annealing. We have seen a higher increase in the characteristic relaxation time for HMW-PC than for LMW-PC when subjected to identical heat-aging treatment in the β-relaxation region. The increase in internal friction is evidently dependent on molecular weight. It would also appear from the results of our collaborators that structural

Table 3. Mean Transition Temperatures and tan δ Magnitudes.

Data Set	Frequency (Hz)	T_γ (°C)	T_γ tan δ	$T_{\beta 1}$ (°C)	$T_{\beta 1}$ tan δ
D1	0.1	−93.7 ± 27.6	0.09 ± 0.02	37.5 ± 9.4	0.06 ± 0.01
D1	1	−90.7 ± 27.1	0.09 ± 0.02	32.0 ± 6.1	0.07 ± 0.02
D2	0.1	−95.2 ± 2.9	0.09 ± 0.01	37.2 ± 6.4	0.07 ± 0.01
D2	1	−91.0 ± 3.8	0.09 ± 0.01	33.8 ± 2.4	0.08 ± 0.01

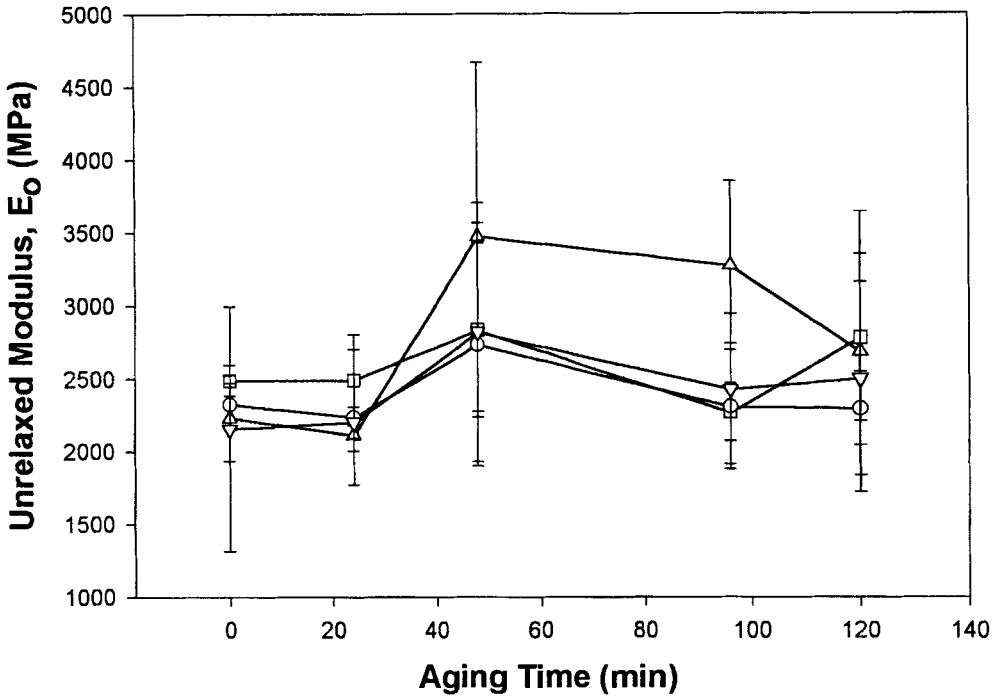


(a)

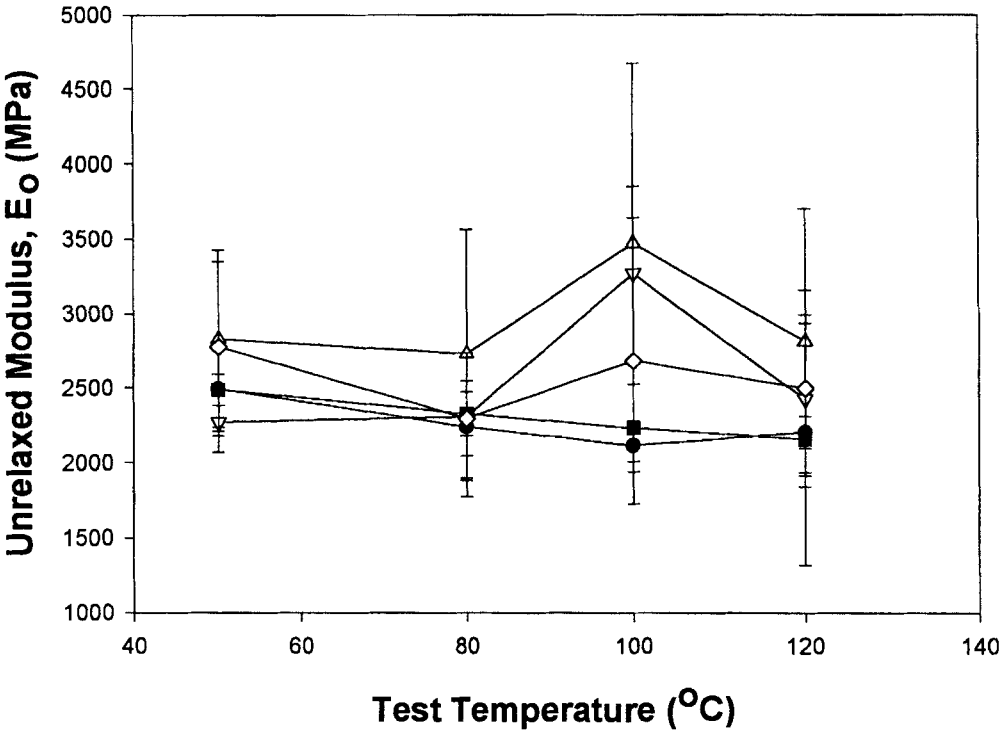


(b)

Fig. 3. The effects of (a) heat-aging and (b) test temperature on the KWW relaxation time constant, τ. Test temperatures for (a) are (□): 50°C; (○): 80°C; (△): 100°C; and (▽): 120°C. Aging times for (b) are (■): unaged; (●): 24 hours; (△): 48 hours; (▽): 96 hours; (◇): 120 hours.

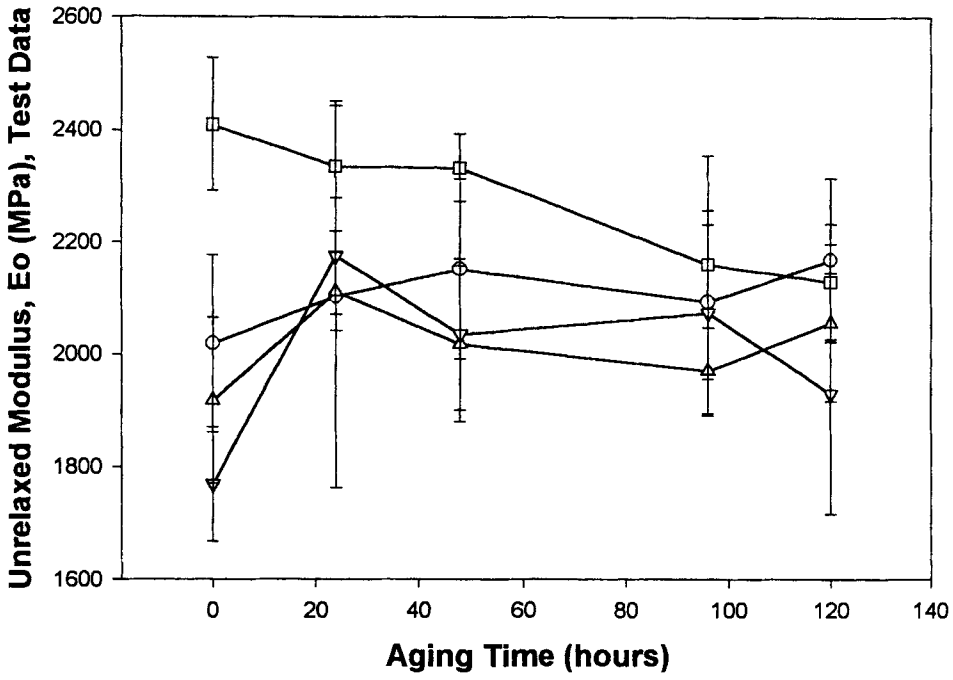


(a)

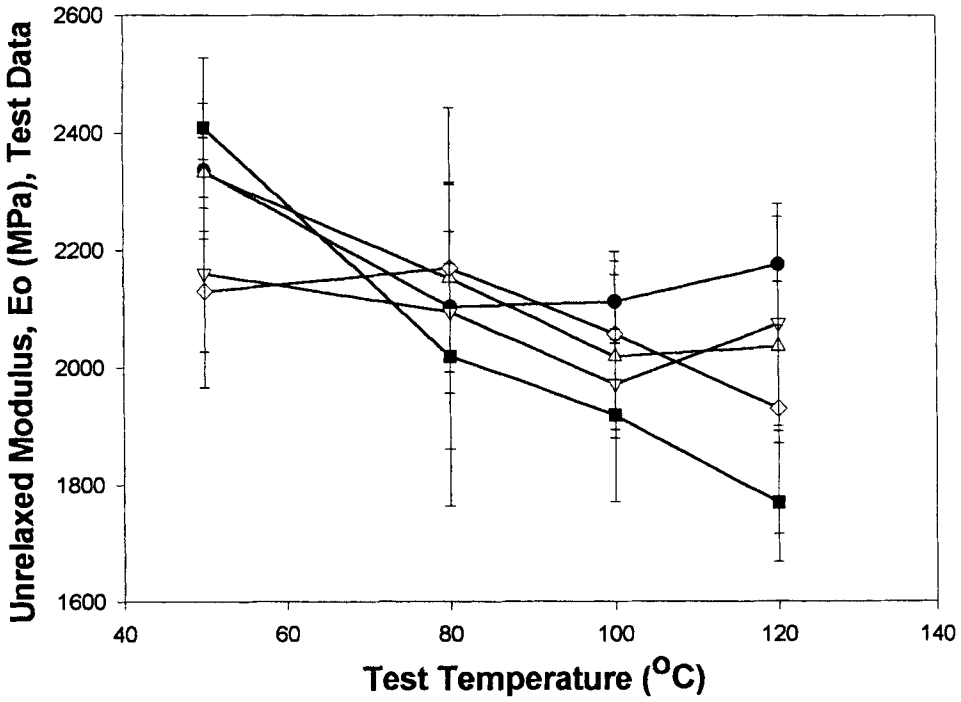


(b)

Fig. 4 . The effects of (a) heat-aging and (b) test temperature on the KWW curve fitted unrelaxed modulus, E_o. Test temperatures for (a) are (□): 50°C; (○): 80°C; (△): 100°C; and (▽): 120°C. Aging times for (b) are (■): unaged; (●): 24 hours; (△): 48 hours; (▽): 96 hours; (◇): 120 hours.

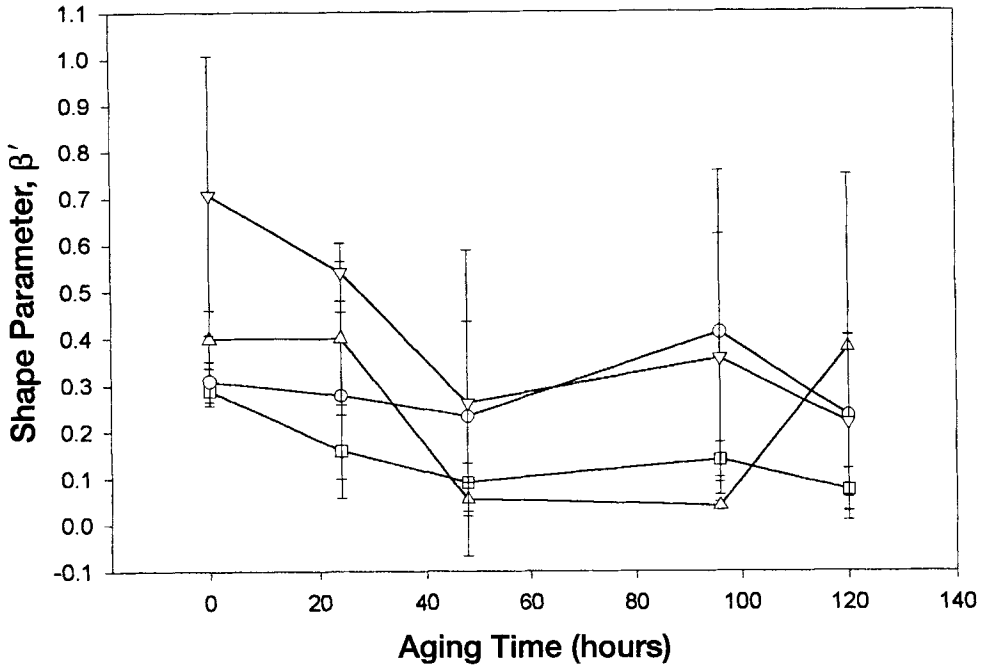


(a)

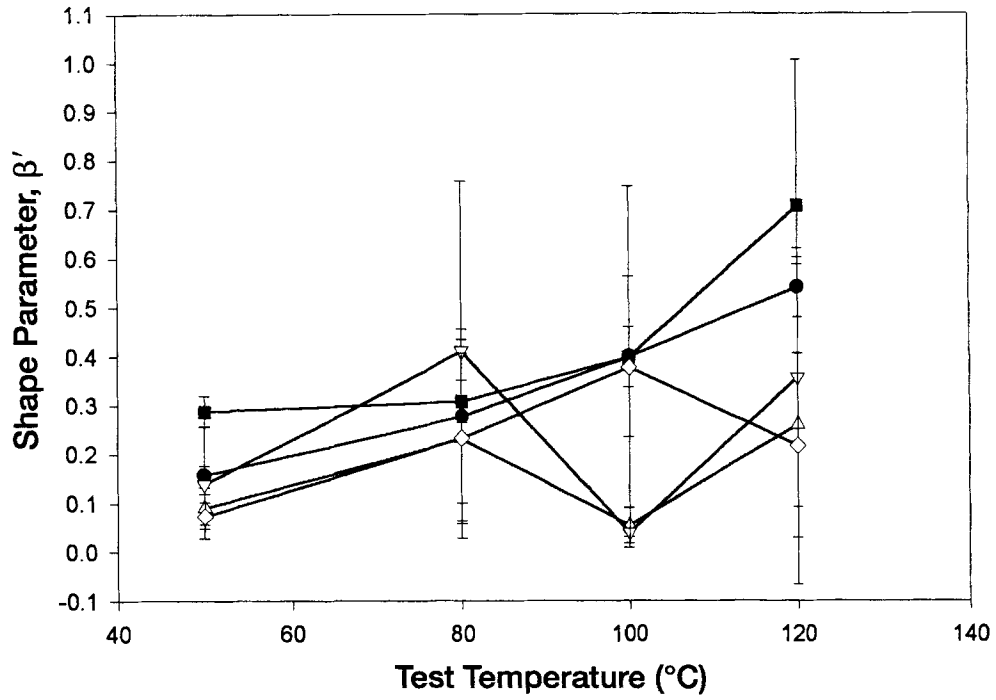


(b)

Fig. 5. The effects of (a) heat-aging and (b) test temperature on the measured unrelaxed modulus, E_{raw}. Test temperatures for (a) are (□): 50°C; (○): 80°C; (△): 100°C; and (▽): 120°C. Aging times for (b) are (■): unaged; (●): 24 hours; (△): 48 hours; (▽): 96 hours; (◇): 120 hours.



(a)



(b)

Fig. 6. The effects of (a) heat-aging and (b) test temperature on the KWW shape parameter, β'. Test temperatures for (a) are (□): 50°C; (○): 80°C; (△): 100°C; and (▽): 120°C. Aging times for (b) are (■): unaged; (●): 24 hours; (△): 48 hours; (▽): 96 hours; (◇): 120 hours.

Table 4. Effect of Heat-Aging on Relaxation Time.

Test Temp.	50°C		80°C		100°C		120°C	
Aging Time (hours)	Mean τ (min)	Standard Deviation (min, %)	Mean τ (min)	Standard Deviation (min, %)	Mean τ (min)	Standard Deviation (min, %)	Mean τ (min)	Standard Deviation (min, %)
0 hours	28512	26563, 93.2 %	98.9	38.4, 38.8%	15.3	1.89, 12.4%	3.6	2.0, 54.6%
24 hours	$7.6 \cdot 10^9$	$1.1 \cdot 10^{10}$ 139.4%	$2.7 \cdot 10^9$	$6.1 \cdot 10^9$ 223.6%	$2.1 \cdot 10^4$	$2.2 \cdot 10^4$ 105.6%	515.9	114.7, 22.2%
48 hours	$1.9 \cdot 10^{10}$	$1.9 \cdot 10^{10}$ 99.6%	$1.0 \cdot 10^{10}$	$1.4 \cdot 10^{10}$ 141.0%	$6.0 \cdot 10^9$	$8.2 \cdot 10^9$ 137.4%	6194.3	9207.1, 148.6%
96 hours	$7.0 \cdot 10^9$	$5.3 \cdot 10^9$ 75.0%	$2.8 \cdot 10^9$	$6.2 \cdot 10^9$ 223.3%	$5.8 \cdot 10^9$	$8.1 \cdot 10^9$ 138.8%	25966.2	50549.9, 194.7%
120 hours	$1.1 \cdot 10^{10}$	$1.0 \cdot 10^{10}$ 97.1%	$6.9 \cdot 10^9$	$7.2 \cdot 10^9$ 104.6%	$4.2 \cdot 10^9$	$9.3 \cdot 10^9$ 223.6%	$1.9 \cdot 10^5$	$3.7 \cdot 10^5$ 196.9%

% = (Standard Deviation/Mean)*100%

evolution caused by heat-aging would almost certainly lead to a loss in fracture toughness (11) but not necessarily be accompanied by a measurable increase in bulk stiffness. This has an important implication in the common practice of using stiffness as a basis for polycarbonate selection in engineering design.

Effects on Shape Parameter, β'

Figure 6a shows a fairly consistent trend with the KWW shape parameter, β', decreasing between 0 and 24 hours aging, and even to 48 hours. There does not appear to be detectable changes beyond these points. Set 1 also shows a trend of increasing β' with test temperature, *Fig. 6b*. The test temperature effect in Set 2 seems different from Set 1. This may be due to the dramatic changes in β' values at 100 and 120°C in Set 1.

The *P*-values in *Table 8* confirm these observations, quantifying a significant aging time and temperature effect for Set 1, and only a test temperature effect for Set 2 results. Although a log transformation improved the heteroscedasticity of Set 2 results, the significance of *P*-values remains unaffected. It is interesting that the results in *Table 8* agree very well with relaxation time (τ) results in *Table 5*. This implies that the β' shape parameter, as τ, may be an indicator of heat-aging effects and state of the recovering structure.

Table 9 shows the calculations for power and number of observations based on the shape parameter mean values and standard deviations. Although the standard deviations and number of observations are still high and the power values remain low for the shape parameter results, they are generally an improvement in comparison to the results for relaxation time in *Table 6*. Moreover, the powers representing the repeatability for the unaged condition are comparably higher than the aged results. From an experimental point of view, the shape parameter is slightly more reliable than relaxation time constant for quantifying the effects of aging and test temperature.

Table 5. *P*-values for Relaxation Time Based on ANOVA Tests.

ANOVA Factors	Set 1 (0, 24 hours); log(log(τ))	Set 2 (48, 96, 120 hours); log(τ)
Aging Time	0.000	0.868
Test Temperature	0.000	0.000
Interaction	0.004	0.681

Table 6. Power and Number of Observations for Relaxation Time Data Repeatability.

Test Temperature	50°C		80°C		100°C		120°C	
Aging Time (hours)	P	N	P	N	P	N	P	N
0 hours	0.079	1778	0.142	309	0.567	32	0.107	35
24 hours	0.068	4290	0.060	10452	0.076	2248	0.261	102
48 hours	0.077	2032	0.068	4014	0.069	3825	0.066	4524
96 hours	0.072	1174	0.061	10039	0.053	3994	0.063	7760
120 hours	0.074	1692	0.076	2229	0.061	10040	0.063	7765

P: Power (α = 0.05)
N: No. of Observations (Power = 0.8)

Table 7. *P*-values for Unrelaxed Modulus Based on ANOVA Tests.

ANOVA Factors	Set 1 (0, 24 hours) E_o	Set 1 (0, 24 hours) E_{raw}	Set 2 (48, 96, 120 hours) E_o	Set 2 (48, 96, 120 hours) E_{raw}
Aging Time	0.149	0.006	0.125	0.323
Test Temperature	0.000	0.000	0.045	0.001
Interaction	0.058	0.020	0.769	0.316

It has been suggested that the β′ parameter may be used to interpret the distribution of molecular relaxations (12). The closer the value of β′ is to unity, the more likely a single relaxation (exponential decay function) is taking place. On the other hand, when the value of β′ is low, a stretched exponential curve is seen that reflects a breadth of distribution of relaxation times due to physically distinct relaxation processes. Thus, the non-exponentiality of β′ with increasing temperature would be a reliable measure of the level of cooperativity. Low values of β′ correspond to the necessity for a high degree of cooperativity and as a result, mobility of a large number of chain segments would be involved. Using this interpretation, our results in *Fig. 6a* would suggest that recovery processes in the unaged state are spontaneous at temperatures within the high-activation region, as proposed in Part I. However, the size of the cooperativity domain (2) increases directly with extent of heat-aging, and even at high temperature, molecular mobility becomes severely restricted. The changes in β′ observed here support the earlier hypothesis in Part I that the reduced mobility in low-molecular weight polycarbonate is also attributed to the lack of intermolecular cooperativity involving several repeat units related to the β-relaxation.

Table 8. *P*-values for Shape Parameter ANOVA Test.

ANOVA Factors	Set 1 (0, 24 hours) β′	Set 2 (48, 96, 120 hours) β′
Aging Time	0.01	0.468
Test Temperature	0.000	0.045
Interaction	0.009	0.142

CONCLUSIONS

The two-factor ANOVA test performed on the dynamic transitions supports the view that the position and magnitude of the α and β_1 secondary relaxations in low-molecular-weight polycarbonate are unaffected by heat-aging. The amount of increase in bulk stiffness caused by heat-aging is weakly dependent on molecular weight. Hence, it is not a reliable indicator of heat-aging phenomena since the increases in stiffness in lower molecular weight material may not be measurable. This is compounded by the fact that there is inherently large experimental scatter in stress relaxation tests.

Repeatability in stress relaxation results for low-molecular-weight polycarbonate is generally poor even at high temperatures. The problem is worsened by heat-aging. This can probably be generalized for glassy polymers since the same levels of error have been observed in the high molecular weight material. Of the KWW parameters computed, the shape parameter, β′, produces the most repeatable results for characterizing relaxation behavior. Moreover, trends for the effects of heat-aging on β′ consistently agree with the relaxation time, τ, values, which suffer very poor repeatability. Thus, β′ may be a better parameter for qualitative comparison in cause-effect studies.

APPENDIX A

Calculations of (i) power and (ii) number of observations for unaged Makrolon 2608, DMA stress relaxation test at 50°C.

(i) H_o: $\mu_o = 28512$; H_a: $\mu_E = 1.10\ (28512) = 31363.2$, $\sigma = 26563$
where: μ_o is the null value, actual sample mean; μ_E is the point estimate; and

Table 9. Power and Number of Observations for Shape Parameter Data Repeatability.

Test Temperature	50°C		80°C		100°C		120°C	
Aging Time (hours)	P	N	P	N	P	N	P	N
0 hours	0.742	20	0.484	40	0.420	49	1	1
24 hours	0.129	390	0.086	1232	0.251	108	0.625	27
48 hours	0.121	457	0.082	1582	0.095	901	0.070	3237
96 hours	0.209	148	0.083	1457	0.264	99	0.090	1133
120 hours	0.100	790	0.088	1143	0.077	1952	0.082	1524

P: Power ($\alpha = 0.05$)
N: No. of Observations (Power = 0.8)

σ is the standard deviation of μ_E, estimated to be equal to the standard deviation of μ_o.

Power = P(T > table value) = P(T > 1.645)
where T = (point estimate-null value)/(standard deviation of point estimate)
1.645 = the 1-sided Student's t Distribution table value for $\alpha = 0.05$

Power = $P((X-\mu_o)/(\sigma/(n)^{1/2}) > 1.645)$
where $X \sim N(31363.2, (26563)^2/5)$,
which assumes the distribution is normal (N)
n = the number of test replicas

Power = $P((X - 28512)/(\sigma/(n)^{1/2}) > 1.645)$

Power = $P((X - 31363.2)/(26563/(5)^{1/2}) + (31363.2 - 28512)/(26563/(5)^{1/2}) > 1.645)$

Power = P(Z + 2851.2/(26563/(5)$^{1/2}$) > 1.645)
where Z = normal distribution Z-table value

Power = P(Z > 1.645 − 2851.2/(26563/(5)$^{1/2}$))

Power = P(Z > 1.405) ~ P(Z > 1.41) =
1 − (0.9207) = **0.0793**

(ii) Power = $P((X - 28512)/(\sigma/(n)^{1/2}) > 1.645) = 0.80$

Power = $P((X - 31363.2)/(26563/(n)^{1/2}) + (313623.2 - 28512)/(26563/(n)^{1/2}) > 1.645) = 0.80$

Power = P(Z + 2851.2/(26563/(n)$^{1/2}$) > 1.645)
= 0.80

Power = P(Z > 1.645 − 2851.2/(26563/(n)$^{1/2}$))
= 0.80
$1.645 - 2851.2/(26563/(n)^{1/2}) = Z(1 - 0.80) = -2.88$
$4.525 = 2851.2/(26563/(n)^{1/2})$
$n = [4.525(26563/2851.2)]^2$
n = 1778 tests

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