

A Computer Implementation of Frequency-Temperature Superposition for Dynamic Mechanical Transformations

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Synopsis

The usual procedure for shifting dynamic mechanical data, involving the construction of a master plot, was compared with a simpler, computer-implemented *double shift* procedure, which obviates the need for such a construction. Data reproducibility indicates that the double shift may successfully be shifted to frequencies greater than one decade to either side of the experimental range.

INTRODUCTION

Modern engineering design applications involving elastomers as structural materials generally require a knowledge of their dynamic mechanical behavior. Too often, the designer is limited by the lack of availability of such data. For the dynamic response calculation of sophisticated systems, such as encountered in aerospace or computer technology, vendor data are insufficient since they usually neglect the rheological behavior of the material, are "typical," and generally noncritical. More reliable data are needed, particularly on damping properties.

Viscoelastic mechanical characterization is generally given as a function of either time or frequency. The frequency-response methods of viscoelastic testing encounter increasing difficulties at frequencies higher than 10^3 Hz, indicating the importance of achieving reliable transformation procedures for shifting low frequency test results to higher frequencies—several decades, if possible.

It was found desirable, in this laboratory, to transform data determined in the 3.5–110 Hz range to substantially higher frequencies. The usual procedure¹⁻³ involves the superposition of such data, obtained over a large temperature range, to form a master plot; this master plot, constructed over a frequency range at some reference temperature, T_0 , may then be shifted to the frequency range corresponding to some new temperature, T , through the use of

$$E'(f, T) = X E'(f_0 [= f \times a_T], T_0) \quad (1)$$

$$X = \frac{T \rho}{T_0 \rho_0} \quad (2)$$

$$\tan \delta(f, T) = \tan \delta(f_0 [= f \times a_T], T_0) \quad (3)$$

TABLE I
Composition of the Butyl Rubber Samples

Material	Parts by Weight
Enjay Butyl 218	100
MPC Black	20
FT Black	10
FEF Black	10
Shellflex 211	6
Antioxidant 2246	1
Stearic acid	1
Zinc oxide	5
MBTS	1
Tellurac	1.5
Spider Sulfur	1
	<hr/> 156.5

where E' is the storage modulus, $\tan \delta$ is the dissipation factor, f is the frequency and ρ the density at temperature T , X is the thermal expansion correction factor, a_T is the shift factor, and the subscript zero refers to the reference state. However, depending on the amount of data and the precision required in the construction of the master plot, this procedure may well become tedious.

Another procedure exists^{1,4} which, as developed in the present work, makes such shifting unnecessary. Since it uses empirically determined a_T values and is easily implemented on a computer, the tedium of the previous procedure is eliminated. Master plots are constructed through eqs. (1)–(3), which are used to transform *temperature*-dependent data at a constant frequency into the required *frequency*-dependent data at any (reference) temperature; the same equations may then be employed to shift the master plot to any other temperature, as with the previous procedure. The present procedure involves, in effect, a *double* shift, as distinct from the more common *single* shift procedure.

The question arises whether, with the simplifications it offers, this double shift procedure suffers in accuracy when compared with the usual procedure. For this reason, a comparison was made, using butyl rubber, an elastomer of current interest in this laboratory. The comparison involved sources of error, data reproducibility, and permissible approximations.

EXPERIMENTAL

Samples

The comparison was made using the butyl rubber whose composition is in Table I. Cure was carried out at 154°C (310°F) for 1/2 hr. Several batches were made and studied in order to ascertain the extent of formulation consistency.

Dynamic Measurements

Measurements were made on a Toyo Rheovibron direct-reading viscoelastometer Model DDV-II. Small sinusoidal strains are applied at frequencies of 3.5, 11, 35, and 110 Hz. On nulling, one obtains both storage modulus and dissipation factor.

RESULTS

Dynamic Data

The storage modulus was obtained at the four Rheovibron frequencies in the temperature range of -70°C to $+50^{\circ}\text{C}$. Using $T_0 = -35^{\circ}\text{C}$, data were successively shifted until a master curve was obtained. This is seen in Figure 1. Note that, although the data should be modified by eq. (2) prior to shifting,¹ this was not done in the present case: we used the approximation $X \approx 1$. The fit in Figure 1 indicates this to be a valid approximation. The values of log shift factor, $\log a_T$, thus obtained were tested by using them to shift the $\tan \delta$ data into a master curve at -35°C . This is also seen in Figure 1. The $\log a_T$ values are plotted versus T in Figure 2. A poor fit of $\log a_T$ versus reciprocal temperature, Figure 3, indicates that its temperature dependence is not described by the Arrhenius equation. A fit to the Williams-Landel-Ferry (WLF) equation,¹

$$\log a_T = \frac{-C_1 \Delta T}{C_2 + \Delta T} \quad (4)$$

where the C 's are constants and $\Delta T = T - T_0$, is substantially better, as seen in Figure 4.

From this plot, it is determined that $C_1 = 7.78$ and $C_2 = 107.15^{\circ}\text{K}$. The form of the WLF equation is temperature invariant, C_1 and C_2 changing as T

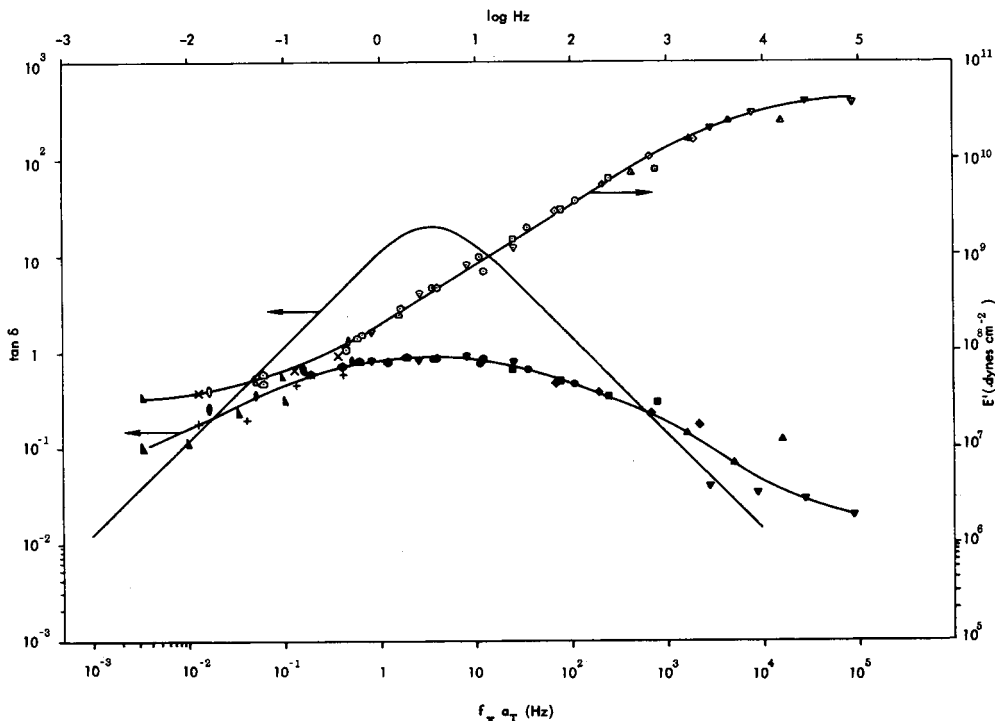


Fig. 1. Master curves for E' (open symbols) and $\tan \delta$ (solid symbols), constructed at -35°C . The $\tan \delta$ curve for a single relaxation time (—) was centered on 3.5 Hz, using lower and upper limiting moduli of 3×10^7 and 5×10^{10} dynes/cm², respectively.

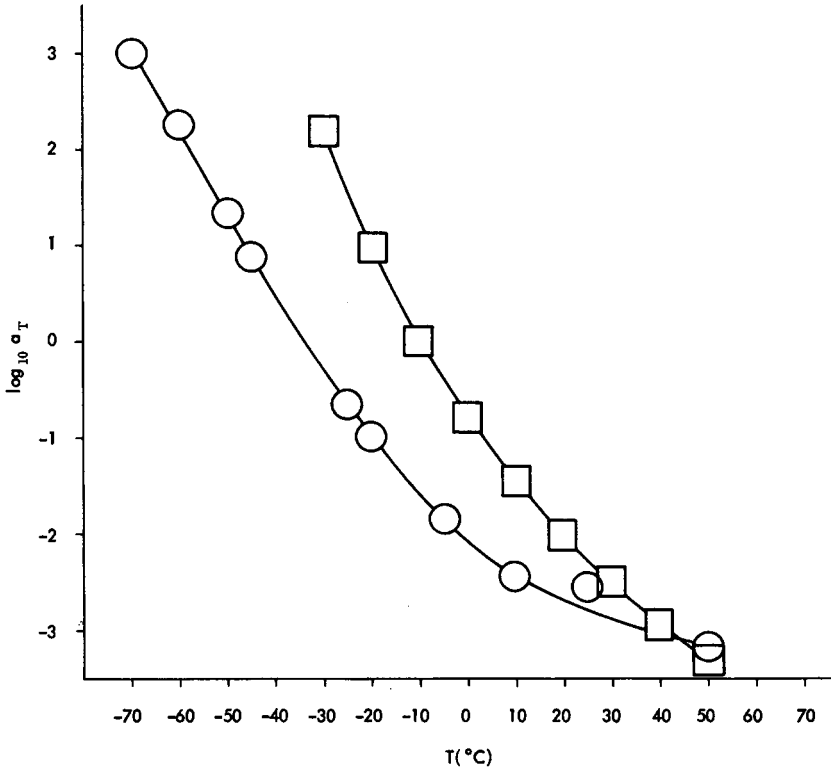


Fig. 2. Temperature dependence of the actual (O) and "universal" (□) shift factors.

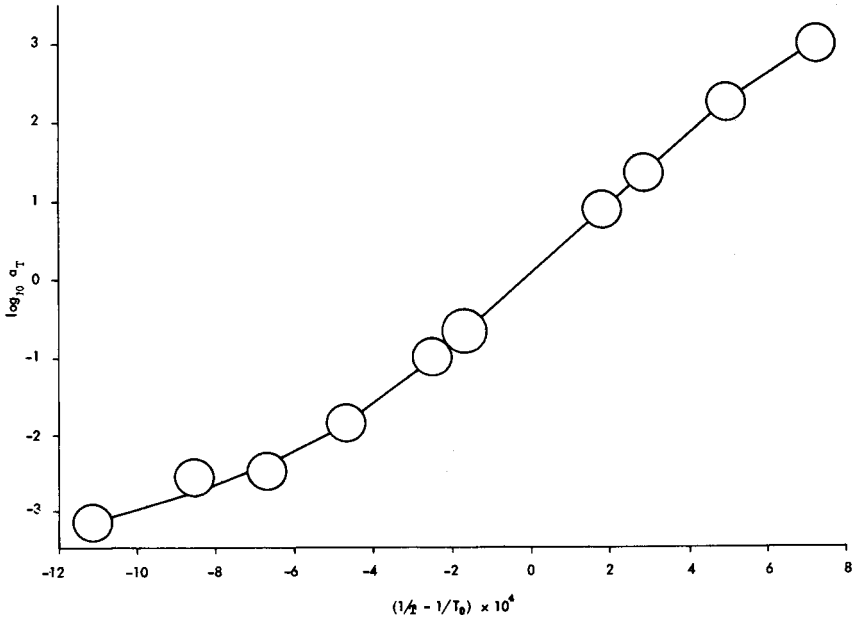


Fig. 3. Arrhenius plot of the shift factor data.

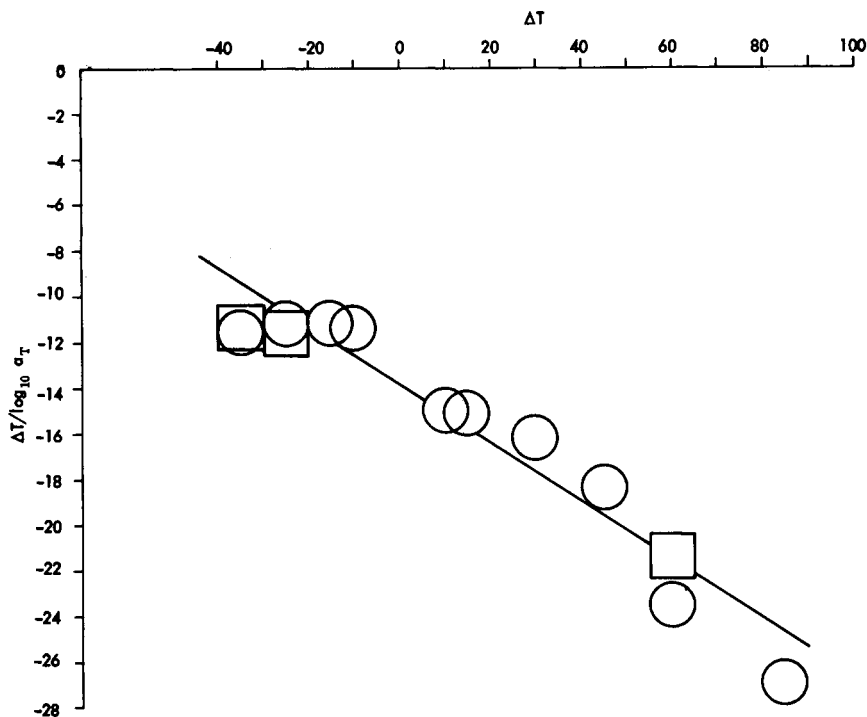


Fig. 4. WLF plot of the actual (O) and smoothed (□) shift factor data.

is changed. There are so-called "universal" values of the constants,⁵ obtained at $(T_0)_{\text{universal}} \approx T_g + 50^\circ\text{C}$. In the present case, T_g was determined by thermo-mechanical analysis to be at -61°C , so that $(T_0)_{\text{universal}} \approx -10^\circ\text{C}$. The values for the "universal" constants at this temperature are $C_1 = 8.86$ and $C_2 = 101.6^\circ\text{K}$. A comparison with the constants determined from Figure 4 ($C_1 = 7.78$ and $C_2 = 107.15^\circ\text{K}$) suggests that, within the temperature range from -35° to -10°C , these values are relatively temperature insensitive. However, as will be seen later, these small differences are significant. Log a_T data determined from the "universal" constants are plotted in Figure 2 for comparison. The shifting of the two curves in Figure 2, without axial rotation, shows them to be identical when $(T_0)_{\text{universal}} = -5^\circ\text{C}$, in good agreement with the presently used value of -10°C .

Shifting Procedures

The commonly used single shift procedure has been adequately described in the literature.¹⁻³ It involves the construction of the master plots in Figure 1 at some reference temperature (-35°C in the present case), the a_T data in Figure 2 necessary to shift to any other temperature, and eqs. (1)–(3). The master plot data were shifted back to 20°C , and are compared with those originally obtained at that temperature in Tables II and III. Similar comparisons were made at several other temperatures. The comparison is quite good, in spite of the fact that, due to the absence of density data, the thermal expansion correction factor used in shifting from -35°C to 20°C was modified to

$$X = T/T_0 = 1.25. \quad (2a)$$

TABLE II
Storage Modulus Data^a Shifted to 20°C

f, Hz	Procedure ^b		Experimental ^c
	Single shift	Double shift	
3.5	4.43	4.1-7.3	4.49 ± 0.61
11	5.23	7.2-16	6.96 ± 0.53
35	7.63	5.7-8.6	7.18 ± 0.43
110	11.8	4.9-13	9.34 ± 0.44
500	27.7	8.1-25	—
2000	65.2	24-40	—
10000	172	49-87	—
50000	467	86-180	—

^a (Dynes/cm²) × 10⁻⁷.

^b Results of a typical data shift.

^c Average.

TABLE III
Dissipation Factor Data Shifted to 20°C

f, Hz	Procedure ^a		Experimental ^b
	Single shift	Double shift	
3.5	0.15	0.26-0.61	0.16 ± 0.04
11	0.25	0.26-0.62	0.23 ± 0.04
35	0.43	0.37-0.77	0.38 ± 0.08
110	0.64	0.34-0.71	0.54 ± 0.06
500	0.86	0.73-0.83	—
2000	0.90	0.80-0.90	—
10000	0.70	0.80-0.86	—
50000	0.44	0.70-0.79	—

^a Results of a typical data shift.

^b Average.

The reason we did not use $X \approx 1$, as when we constructed the master curve, is that there the construction involved the shifting of data, to T_0 , from temperatures ranging from very close to T_0 to temperatures somewhat removed. For low values of ΔT , at least, $X \approx 1$ constituted a good approximation. In the present situation, the data are to be shifted a full 55°C, over which $X \approx 1$ is no longer a good approximation. The point we wish to make is that, in lieu of the actual correction factor, the lack of density data forces the use of the modified correction factor in eq. (2a). Tables II and III indicate that, over this large temperature span (55°C), eq. (2a) constitutes a reasonable approximation.

The double shift procedure lends itself to data obtained over limited frequencies: although the Rheovibron is limited to but four frequencies, it may be operated over a large temperature range. Such *temperature*-dependent data may be transformed into *frequency*-dependent data^{1,4} through a knowledge of $\log a_T$ values between the temperatures of measurement and some reference T_0 . Thus, this procedure makes use of the "universal" values of both a_T (Fig. 2) and T_0 (-10°C), along with eqs. (1)-(3), to transform *temperature*-dependent data at some constant frequency into *frequency*-dependent data at -10°C; the master plots so constructed may then be shifted to any desired temperature, as with the usual procedure. Such data, similarly shifted to 20°C, are also found in Tables

II and III. Note that the double shift procedure gives ranges of values. This is because the data at any temperature are *frequency*-dependent. Although this will be considered in the next section, it is well to note that the experimental values obtained at 3.5 Hz lie closer to those obtained by transforming the 3.5 Hz data (minimum values in Tables II and III); similarly, the experimental 110 Hz values lie closer to those obtained by transforming the 110 Hz data (maximum values).

DISCUSSION

Comparison of Shifting Procedures

The major difference between the two procedures described here is in the construction of the master plot which will subsequently be shifted. Any comparison between them must then consider the errors involved in constructing this plot.

The single shift procedure is prone to six possible sources of error: first, the Rheovibron machine correction, used in calculating E' , has been taken as temperature invariant, in accordance with the manufacturer's directions. A recent study⁶ has shown the machine constant to be sufficiently temperature dependent to introduce errors in E' at temperatures sufficiently far from that at which the machine correction was determined.

Second, it is implicit in the shift procedure, as well as in the construction of the master curve, that the relaxation time be constant. Although enough experimental data have been accumulated over the years to ensure that all relaxation times vary identically with temperature, a $\tan \delta$ plot for a single relaxation time, seen in Figure 1 centered about 3.5 Hz, indicates on comparison with the actual data that we are dealing with a spectrum of relaxation times. Such a spectrum is known to vary with temperature,⁷ introducing an error in proportion to the extent of the variation.

Third, there are inherent sighting errors in the construction of the master curves. Fourth, eq. (1) was used for shifting with a modified correction factor. Fifth, one must consider the validity of eq. (1) to perform data shifts on the master curves. In light of the phenomenologic nature of this equation^{1,7,8} and its sometimes limited applicability,¹ this has to be evaluated on an individual basis. Finally, one must consider the validity of approximating the correction factor as $X \approx 1$, as was done in constructing the master curve; the validity of this approximation must surely decrease as ΔT becomes larger. In the present case, considering Figure 1 and the comparison of experimental data with Tables II and III, it would seem the errors are minimal or tend to cancel.

Except for the sighting error, one might reasonably expect those errors in this procedure to be magnified in the double shift procedure, since not only does the latter involve two shifts, but one of these shifts involves converting from a *temperature*-dependent domain into a *frequency*-dependent domain. This expectation appears to be borne out in Tables II and III, in which the usual procedure gives values of E' and $\tan \delta$ gratifyingly close to the experimental values while the double shift procedure gives ranges whose maxima or minima may differ significantly from experiment. This latter phenomenon is due to the limitations of the procedure in transforming temperature-dependent data into frequency-dependent data. This, in turn, is due to the assumption in the tem-

perature-frequency interconversion that the initial temperature-dependent data are frequency invariant. Such an assumption is clearly invalid. Its application leads to a difficulty described in the previous section: with the double shift procedure, there is a close correspondence between the 3.5 Hz experimental data and the *minima* obtained at 3.5 Hz since these latter values were obtained by transforming the experimental 3.5 Hz data. For the same reason, the experimental 110 Hz data correspond with the 110 Hz *maxima*. This correspondence of data at a given frequency with only those data originally obtained at that frequency must be considered a limitation of this procedure.

However, one should not lose sight of the fact that while the single shift procedure is available only through an actual construction of the master plot, the double shift procedure makes a computer construction of the master plot using raw Rheovibron data. The advantage of computer construction cannot be overemphasized, not only in its speed, but in its ability to alleviate tedious work.

Frequency Extensions

Although the upper frequency of the experimental data is 110 Hz, the shifted data have been extended to 50 kHz in Tables II and III. This was done to study the predictability of the procedures at frequencies significantly different from those in the experimental domain. Although our comments are confined to frequencies above experimental, similar comments will apply to those below.

Because of the accuracy of the single shift procedure in reproducing the experimental data, we consider that this procedure represents the data reasonably well at frequencies considerably higher than 110 Hz, although it is by no means suggested that this holds to 50 kHz. A comparison of the data generated through the two procedures is instructive.

Table II indicates that, within a decade increase above the experimental frequency, the *maximum* double shifted E' value is still within the experimental precision of the E' value obtained by the single shift procedure, although shortly thereafter it begins to decrease. Table III indicates a similar range for $\tan \delta$, after which its magnitude is larger than that obtained by the single shift procedure. This divergence appears due to two causes: first, the WLF constants determined by eq (4) differ from the "universal" constants. Although both represent the *experimental* data, they may differ considerably outside the experimental range. Note that, if Figure 2 were replotted versus ΔT , the two curves would superimpose reasonably well within the experimental temperature range but would diverge outside. Second, as described in the previous section, double shifting gives best results when the experimental data are transformed back into their original frequency. Thus, higher transformed frequencies would be expected to give somewhat lower E' values. The double shift procedure appears to have the following limited applicability: in extending to higher frequencies, the data obtained at the *highest* experimental frequency may be shifted at least one decade before the E' and $\tan \delta$ values deviate significantly from those obtained by the usual procedure. Similarly, in extending to lower frequencies, the data obtained at the *lowest* experimental frequency may be shifted at least one decade.

CONCLUSIONS

A comparison of two methods of shifting dynamic mechanical data to other temperatures and frequency ranges has shown that the simpler double shift procedure gives data comparable to the more tedious single shift procedure at frequencies at least one decade to either side of the experimental range.

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