

New Approach to Investigate the Dynamic Relaxation Process of Complex Peak in Mechanical and dielectric Characteristics of Anelastic Solids

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Abstract - Complex dynamic relaxation processes of mechanical as well as dielectric character in polymeric anelastic solids are closely related through the movement of molecular chain segment in morphological structure, and the morphology can easily be modified by the treatments such as mechanical drawing or irradiation, those of which result, in turn, the complicated change on the appearance of the observed complex relaxation peak. In order to extract any meaningful understanding from the modified appearance of the peak, the relaxation peak must be resolved into the sum of the dynamic single relaxation peaks, each of which can be characterized respectively by three factors such as activation energy, magnitude of peak height and peak point temperature on the temperature dependent characteristics.

1. INTRODUCTION

The dynamic relaxation process of mechanical and dielectric characteristics in anelastic solids are sensitively related to the morphology of the inner structure in solids, and the observed frequency (ω) or temperature (τ) dependent characteristics are usually consisted of the sum of both single and complex relaxation peaks, in which single or multiple numbers of relaxation time are distributed. Furthermore, the shapes of those peaks are deformed easily whenever the solids is subjected to morphological changes by the treatments such as mechanical drawing or irradiation and the deformation seems to complicate so much that any meaningful information is hardly drawn out systematically from the resulted appearance.

As an illustration, Fig. 1 shows the overall mechanical damping characteristics - that is the logarithmic decrement of internal friction - measured by Kê type torsion pendulum on a kind

of low density Polyethylene. Figure 2 describes the comparison of the mechanical damping of another as-received change as a function of temperature measured by Kê type torsion pendulum, on a kind of low density PE specimen

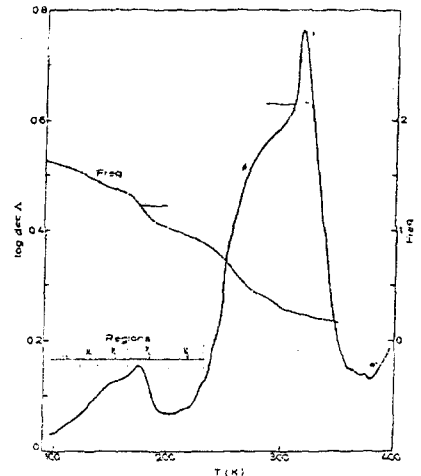


Fig. 1. Characteristics of the over-all mechanical damping spectrum and frequency

with that of the same material extended mechanically to ca. 4 times.

2. THEORY AND DISCUSSION

Under the assumption that any given dynamic complex relaxation peak [1-3] can be resolved into finite numbers of dynamic single relaxation component peaks, the purpose of this paper is to develop the procedure to accomplish the proposed decomposition, and finally the comparison is tried between original curve and the recomposed one with the obtained components of single peak. The decomposition principle is to settle down the acceptable initial single component peak, at first, on the proper place of the complex peak, and then peels off the former from the latter. The outline of the next neighbor peak can automatically be estimated from the shape of the resulted remains of the proposed procedure.

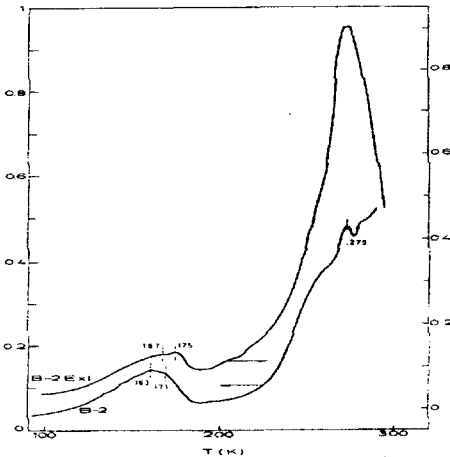


Fig. 2. Comparison of mechanical damping behavior of as received specimen with that of the same material extended to ca. 4 times.

However, as is known in general, the very close formulaic similarities [4] in expression exist between mechanical and dielectric relaxation process of anelastic solid, and, for instance, both

cases of dynamic single relaxation peak. As are proportional to $J''(\omega)$ (or $G''(\omega)$ and $\epsilon''(\omega)$), respectively, where each of those represents the imaginary part of complex compliance (or modulus) and dielectric constant being expressed as

$$J''(\omega) \text{ or } \epsilon''(\omega) = \text{relaxation strength} \times (\omega \tau / 1 + \omega^2 \tau^2)$$

$$\text{and the relaxation time } \tau = \frac{1}{V_0} \exp \frac{W}{RT}$$

Were, V_0 : attempting frequency

W : activation energy, and R : gas constant

Letting $\ln(\) = Z$,

$$\frac{\omega \tau}{1 + \omega^2 \tau^2} = \text{sech} Z \cong e^{-|Z|} \quad \text{for } |Z| \geq 2,$$

therefore,

$$A_s = A \text{ sech} Z \quad \text{or}$$

$$\ln A_s = \ln \left(A \frac{\omega}{V_0} \right) + \frac{W}{RT} \quad \text{for } |Z| \geq 2,$$

Accordingly, activation energy can be estimated from the inclination of the linear part, say as wing, for large Z on $\ln A_s$ vs $1/T$ plot. In advance to locate the initial single component peak to the given complex peak, A on $\ln A$ vs $1/T$ plot, it is necessary to clarify several factors related to the single peak such as the better peak point temperature which is less affected by the wings of neighbor peaks, activation energy which decides the breath of half-width, and magnitude of the single peak. For the decision of the better peak point temperature, it is effective to utilize the rapid decreasing character of half-width in $\text{sech} Z$ as increasing the order of derivatives. Figure 3 shows the behavior of hyperbolic secant function and its derivatives. As the result of examination on $\text{sech} Z$, the use of the sixth derivatives is enough for the present purpose. Figure 4 presents the behavior of the sixth derivative of $\text{sech} Z$ and the relative magnitude of half-width vs. derivative order.

In the course of the procedure to determine the better peak point temperature, another useful information such as the nearest concave or

inflection points at both sides of the determined peak point can automatically be found and, as the first approximation, those points must be regarded locate - the slope represents the activation energy of the initial peak - can be estimated from those points. Table 1 expresses an example of the use of difference test in the each of derivative order.

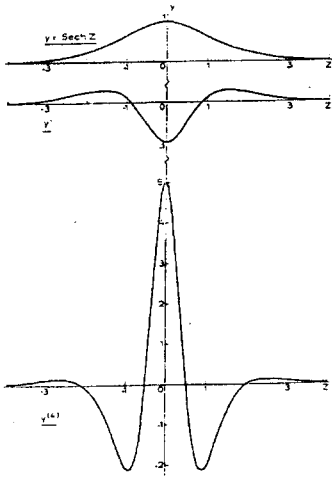


Fig. 3. Behavior of sech Z function and its derivative

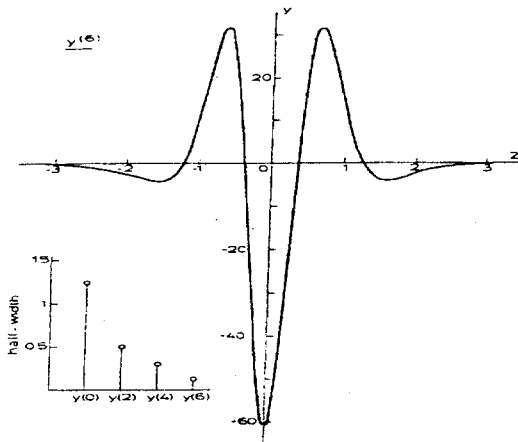


Fig. 4. Behavior of the 6th derivation of sech Z.

For the estimation of the magnitude on the component peak, determine, at first, the shape of

the unit strength component peak, sech Z with the same activation energy being found, on the same scale of graphic paper in use and then, locate the shape overlapping the inclination and the peak point temperature axis to those being found already. The distance between the top point of peak axis and that of sech Z corresponds to the magnitude of the component peak. After finishing to locate the initial unit strength component peak, peel off this peak from the given complex peak.

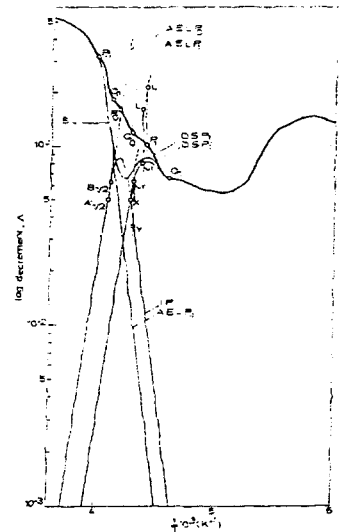


Fig. 5. The analyzing method

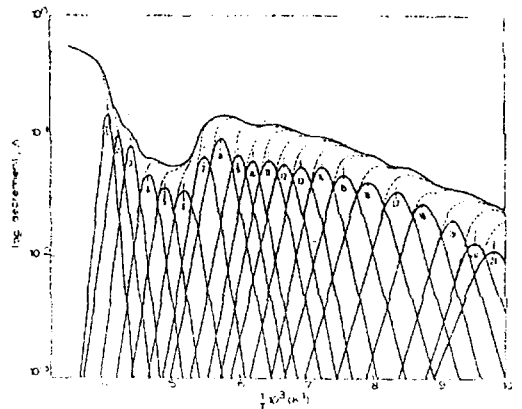


Fig. 6. Constituent peaks in 7 regions of the as-received specimen using the analyzing method.

Then the inclinations of both sides of the next neighbor peaks can automatically be approximated from the resulted remains of the figure. At this place some refinement should be taken to the slope of the initial peak by taking the consideration of the resulted inclination of the neighbor peak. Repeating this procedure, the information of the component peaks can be obtained one by one. Figure 5 shows the initial stage of analyzing method, and figure 6 presents the constituent peaks in β regions of the as-received specimen obtained by the proposed analyzing method. Also Table 2 collectively indicates the data for activation energy, peak temperature and peak height of the individual component peak. Figure 7 shows the comparison between the original curve and the recomposed one from the obtained data.

Table 2. Collective indication of activation energy, peak temperature and peak height of the individual component peak.

peak Number	Ea kcal/mol	peak temperature		Peak height (Δ)
		$(1/T) \cdot 10^3 (K^{-1})$	T(K)	
1	28.5	4.04	248	0.150
2	22.5	4.20	238	0.100
3	22.0	4.40	228	0.084
4	18.0	4.68	214	0.046
5	17.0	4.89	205	0.038
6	16.0	5.21	192	0.034
7	16.0	5.48	183	0.064
8	14.0	5.72	175	0.100
9	14.0	5.98	167	0.069
10	14.0	6.21	161	0.060
11	12.5	6.44	155	0.060
12	12.0	6.67	150	0.059
13	12.0	6.94	144	0.055
14	11.5	7.26	138	0.054
15	10.0	7.58	132	0.047
16	9.25	7.94	126	0.041
17	9.25	8.36	118	0.034
18	9.25	8.77	114	0.028
19	9.25	9.18	109	0.020
20	9.25	9.52	105	0.014
21	7.00	9.80	102	0.012

Table 1. An example of difference test in the each of derivative order.

$(1/T) \cdot 10^3$	reading	1st	2nd	3rd	4th	5th	6th
4							
50	3.20						
52	60.4.00						
54	30	40					
56	60	40	0	-10	20		
58	90	30	-10	10	-10		
60	30	0	0	0	-30	40	
62	5.20	30	0	0	-15	10	-25
64	35	30	0	-15	30	-15	60
66	50	30	-15	15	-15	45	-90
68	65	15	0	0	-5	-45	55
70	75	15	0	-5.5	10	5	
72	85	15	-5.0	-5	-10	15	-35
74	90	10	-5	0	5	-20	35
76	90	10	-5	0	9	15	-20
78	85	5.0	-3.3	8	-8	-5.8	13
80	83	-5.2					

3. CONCLUSION

(1) As suggested by the respective treatment of Rouse [1], Buche [2], and Zimm [3] of molecular theories on the relaxation of anelastic and dielectric effects in polymeric solids, the complex dynamic relaxation process can possibly be expressed by the sum of the single relaxation process with the discrete value of relaxation time, so that the proposed graphical resolving method has to be recognized to stand on the firm theoretical basis.

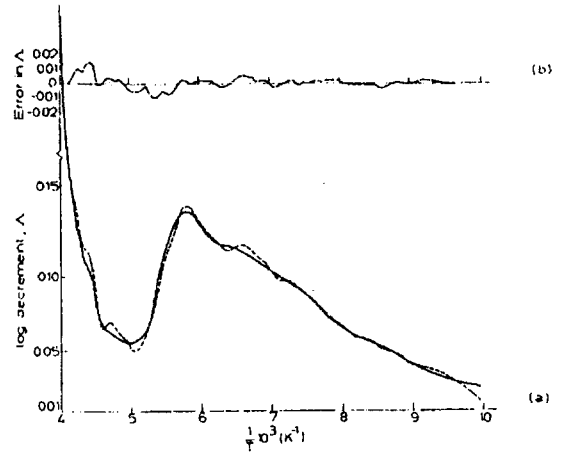


Fig. 7. comparison between the experimental result and the recomposed curve from the data

(2) The single relaxation peak as the component of a complex peak has to be specified with three factors such as activation energy, magnitude of peak height and peak point temperature on the temperature dependent complex relaxation characteristics, and a series of discussions related to determination procedures are introduced for the determination of those factors.

(3) For illustration purpose, β peak of the internal

friction measured on a low density polyethylene is employed which may be regarded as the complex mechanical relaxation peak originated by the dynamic movement of side chain in molecular chain structure under the alternative stress field, and as the result of comparison it is known that the resultant curve recomposed by a series of the obtained single component peaks shows good agreement with the original one.

(4) The proposed hand resolving procedure to obtain single component peak is so laborious that the establishment of proper programming is quite necessary for the computerization of the procedure.

(5) The proposed techniques may be expected to use possibly as a means for the study on the correlation between mechanical properties and dielectric ones on polymeric solids.

4. REFERENCES

- [1] P. E. Rouge: J. Chem. Phys., 21, 1271 (1953)
- [2] F. Bueche: J. Chem. Phys., 22 . 603 (1954)
- [3] B. H. Zimm: Anelastic and Dielectric Effects in Polymeric Solids, pl52, N. G. McCrum et al, John Wiley & Sons. London
- [4] ditto; p7-14

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