NOTES

Methods for the Simultaneous Measurement of Continuous and Intermittent Stress Relaxation of Rubber Vulcanizates

Two recent books[1,2] on the degradation and chemorheology of polymers both have chapters describing two closely related methods[3,4] of carrying out continuous and intermittent stress relaxation measurements simultaneously on the same specimen of rubber vulcanizate. They are modifications of A. V. Tobolsky's classical procedure from 1944–1946.[5] The presentation of the two methods in these books leaves the impression that only the second one[4] is a "simultaneous" method and generally applicable to all kinds of rubber vulcanizate. This is not the case. Furthermore, the theory of the authors needs some corrections and comments.

The first modification to be published was that by Ore in 1955,[3] in which the intermittent relaxation measurements are modified by making them part of the continuous stress relaxation experiments, i.e., by determining intermittently the change in apparent tangent modulus. This can be done by subjecting the continuously relaxing specimen to a small additional stress intermittently and quickly measuring the corresponding increase in elongation. With a suitable stress relaxation apparatus, this is easily and accurately done by means of a fixed cathetometer microscope with a built-in scale. This procedure seems less disturbing to the experiment as a whole than would be the case with large additional intermittent extensions. As pointed out in the article, making both types of measurement simultaneously and on the same sample halves the time of experiment and avoids variation in sample and conditions. Obviously, the apparent tangent modulus can also be measured with a strain gauge or electromagnetic compensation-type apparatus in which the measuring unit or the lower specimen holder can be given small but accurate intermittent displacements. This first modification of Tobolsky's method developed from the need for a method which could be used on certain pure gum peroxide vulcanizates which were too weak to tolerate large intermittent elongations.[6] In addition to being a very useful method for ordinary vulcanizates, it was almost indispensable for the study of such weak rubbers. The two figures (4.2 and 4.3) reproduced in both books show the excellent agreement between this and Tobolsky's method. These relaxation curves are obtained (as should be apparent from the original article[3]) by the "simultaneous" procedure and with ordinary sulfur vulcanizates.

The second modification was that by Sobue et al. in 1964,[4] which differs from the above mainly in using comparatively large additional extensions and measuring the corresponding force. They found this more convenient in their strain gauge-type of relaxation apparatus. However, it is misleading when these authors use the designation "simultaneous (or SMCIR) method" as if it only applied to their own modification and not to the tangent modulus method. The latter method has already all the advantages over Tobolsky's method which the authors claim for their modification.

It should also be pointed out that in changing from real stress in their original article[4] to force per unit cross-sectional area of the original unstrained sample in the two books, the authors do not take into account the effect of this on the last term of eq. (4.14). This term represents the contribution from crosslinks formed at the continuous extension ratio α_1. It should be corrected by a factor $1/\alpha_1$ because this new network has a smaller cross-sectional area in its relaxed state than has the remaining part of the original network (first term). There are also printing errors in the formulae, but they are obvious.

The values of the relative increase in crosslink density, $\Delta C(t)/C(0)$, during the relaxation experiments have been recalculated from the relaxation curves presented. They were found to be in considerably better agreement with the values obtained by Tobolsky's method (up to 50% relaxation) than appears in the original article and the books.

A further correction is, of course, required in order to take into account the deviation of the stress–strain relation of real rubbers from the theoretical $f = G(\alpha - 1/\alpha^2)$. This correction depends on both the continuous and the comparatively large intermittent extension ratios in the second modification. The corresponding effects have been taken into account and discussed in the article[3] on the simultaneous method of continuous stress and intermittent tangent modulus relaxation measurements.

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References

1. K. Murakami, in *Aspects of Degradation and Stabilization of Polymers.* Elsevier, New York, 1978, p. 362.
2. K. Murakami and K. Ono, in *Polymer Science Library* 1: *Chemorheology of Polymers.* Elsevier, Oxford, 1979, p. 116.
3. S. Ore, *J. Appl. Polym. Sci.*, **2**, 318 (1959).
4. H. Sobue, K. Murakami, et al., *Chem. High Polym. Jpn.*, **21**, 606 (1964) (in Japanese).
5. A. V. Tobolsky, *J. Appl. Phys.*, **27**, 673 (1956).
6. S. Ore, *On the Oxidative Stress Relaxation of Natural Rubber Vulcanized with Di-*tert*-butyl Peroxide.* Oslo U. P., Oslo, 1958.

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