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PHYSICAL AGING AND THERMAL HISTORY EFFECTS IN PVC, BOTH ABOVE AND BELOW T_G

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Abstract - Mechanical and dielectric properties of rigid PVC depend on time (physical aging) and thermal history. It is discussed how, in the physical characterization of PVC, these phenomena should be accounted for in order to obtain reliable results.

In practical processing, plastic articles are generally made by moulding at high temperatures followed by fixation of the shape by rapid cooling to below the glass transition temperature T_g, the idea being that the (amorphous) plastic solidifies and attains glass-like rigidity on passing T_g.

As has been known for many years (Ref. 1), the above mentioned idea is only partially correct. The solidification is not actually completed within the short cooling period through the T_g--range, but continues for many years during the practical life and use of the plastic product. The material is therefore said to age physically; its stiffness, creep resistance, brittleness, etc., increase, whereas its mechanical damping, dielectric loss, D.C. conductance, etc., decrease.

Some years ago, we studied this aging for a wide range of polymers (Refs 2, 3), one of them being rigid PVC, Using primarily the data of Ref. 2 and Ref. 3, we will point out here how this aging influences the physical characterization of PVC. We consider the following subjects:

1. Small-strain creep or stress relaxation

The results of a creep test are strongly influenced by the aging period preceding the test*. For example, for PVC at room temperature, an increase in aging time from 1 hr to 1 year induces changes in the creep properties which are as large as those produced by a change in temperature of at least 40 °C. The parameter aging time has thus to be included in the specification of the material properties, just as parameters such as temperature, stress level, etc..

Since at small strain, the creep and stress-relaxation behaviour is intimately linked by the equations of the linear viscoelastic theory (Ref. 4), the above conclusion also applies to stress-relaxation (*cf.* also Ref. 5).

2. Creep at larger strains (up to a few percent)

The effect of previous aging appears to become less pronounced when the creep tests are performed at high levels of stress, the reason being that the "structural" changes occurring during creep overshadow and erase those which occurred during the previous aging period. Yet, at practical strains of, say 0.5-1%, the aging effects are still quite important.

3. Distinction between momentary and long-term properties

Because the material ages, one has to distinguish between two kinds of properties. Tests which are short as compared with the previous aging time yield the "momentary properties" of the aging material. Any changes in the material properties during testing can be neglected; the test results depend on the previous aging time in a simple parametric way. For tests lasting long compared to the previous aging time, considerable aging will occur during testing, i.e. during the performance of the test, the material properties will change with time, just as in the case where during testing the temperature is varied. The properties determined with such long-term tests are essentially different from the above defined momentary properties.

*Except when indicated otherwise, all statements given in this paper are based on the results of Ref. 2.

4. Methods for predicting long-term creep, stress-relaxation, shrinkage

The actual long-term behaviour of many plastic products is of the kind described above; i.e. the behaviour is affected by simultaneous aging. The methods for predicting long-term behaviour on the basis of tests of short duration therefore had to be reconsidered. This problem has been solved for creep, stress-relaxation and shrinkage due to internal stresses. The new prediction methods allow for extrapolations on the time scale by a factor of 100 or more, and their results differ considerably from those obtained by the usual prediction methods. Particularly, the procedure of accelerating tests by using higher temperatures has been proved unreliable.

5. Effect on dynamic mechanical properties

Aging produces a decrease in damping tan δ (by up to a factor of 2 for PVC), but this effect is restricted to the temperature range between the secondary loss peak ($\sim$ -50 °C at 1 Hz) and the glass transition temperature.

6. Complicated thermal history and annealing effects

The aging process is a structural relaxation with a wide distribution of relaxation times (Refs 2, 6, 7, 8). As a consequence, a complicated, almost confusing behaviour is observed when the temperature is cycled or otherwise changed in a non-monotonic way. The behaviour resembles secondary crystallization, in which a structure formed at temperature T is destroyed and replaced by another on heating to a temperature T' > T (Ref. 9). Some examples are the following: Fig. 96 of Ref. 2 refers to two identical PVC specimens aged at 20 °C for different times. At 20 °C the creep curves differ considerably, but on heating to 50 °C, these differences are erased, and the two samples show identical behaviour. Fig. 97 of Ref. 2 refers to the effect of annealing at 60 °C on the yield stress σ_y at 35.5 °C. Since heating primarily destroys the "structure" formed during the previous storage of the sample at room temperature, the prime effect of annealing is to reduce σ_y and to remove the endothermic DSC peak at T_g. It is only after longer times of annealing at 60 °C that the new "structure" characteristic of the temperature of 60 °C begins to dominate and to raise σ_y as well as the height of the DSC peak. Figures 98 and 99 of Ref. 2 refer to the loss properties (tan δ) at 1 Hz. Clearly, the samples as received (stored at 23 °C for several months) behave as aged materials at low temperatures and as quenched materials at high temperatures. The explanation is that the "structure" formed during storage at room temperature is destroyed by the heating during the torsional pendulum run. More data on such complicated thermal history effects are given in Fig. 100 of Ref. 2.

7. Effect on electrical properties

The same aging effects as found in the mechanical creep properties should be expected for the dielectric relaxation. This has been confirmed by experiment (Refs 2, 10-12). Further removed from mechanical creep is DC conduction, particularly electronic conduction; however, aging appears to influence DC conductivity too (Refs 2, 11).

8. Effect on yielding, necking, shear banding and crazing

There is a growing body of evidence (Refs 2, 13, 14, 15) that the "structure" formed by aging has to be destroyed before yielding can take place. In this respect, a glassy polymer appears to behave thixotropically. Owing to the original "structure" first having to be destroyed, the stress-strain diagram shows an overshooting peak, not only in tension, but also in shear or uniaxial compression. This overshooting (yield drop) leads to strain localization (Refs 16-19) in the form of necks, or, when stress concentrations are present, to shear banding and crazing before gross yielding. In this connection, it should be noted that freshly quenched PVC may deform uniformly in tension at room temperature, without showing necking or crazing. Consequently, aging appears to affect strength and ductility by determining the propensity for strain localization.

9. Aging of PVC above T_g

For purely amorphous polymers, such as atactic PS, significant aging effects are only observed at temperatures below T_g. In semi-crystalline polymers and filled rubber systems, physical aging is also observed above T_g, which could be explained with the model of an extended glass transition (Ref. 2). It is assumed that, in their immediate vicinity, the hard particles or crystals reduce the mobility of the amorphous phase, so that the material actually possesses a wide distribution of T_g's. This explains the aging above the "gross T_g" as being due to those parts of the amorphous phase which, at the measuring temperature, are close to their glass transition. Rigid PVC is not completely amorphous, but has a low degree of crystallinity. We have therefore investigated the physical aging from 80 to 150 °C, and found that it substantially affects the small-strain creep properties.

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