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Book Review

Physical Aging in Amorphous Polymers and other Materials, by L.C.E. Struik, Elsevier Scientific Publishing Company, Amsterdam, 1978, 230 pp., Dfl.135.00.

This book is unusual in that it provides the description of a single project, conducted between the years 1962 and 1976 at the Central Laboratorium TNO and sponsored by a large group of industries. First it must be noted that the word amorphous refers to a state which nobody is very keen to define. The old-fashioned definition was that the amorphous state was a non-crystalline solid, energy rich and in a metastable state. This was blown sky high by the ability of X-ray diffraction techniques, and then electron diffraction techniques to establish structure in smaller and then smaller crystals so the idea of a non-crystalline solid, the first criteria in the above description disappears. The present work specifically refers to polymers, side steps a direct definition of amorphous but starts from the concept that amorphous solids are not in thermodynamic equilibrium at temperatures below their glass transition and should be regarded as supercooled liquids whose volume, enthalpy and entropy are greater than they would be in the equilibrium state.

The project employs various measuring techniques which are described in Appendices to the main body of the book. In most of these techniques a certain property is measured usually with reference to time and temperature. Details are given of volume dilatometry, length dilatometry, the torsion pendulum, torsional creep equipment, short-time and long-term tensile creep equipment and measurement of charpy impact and tensile impact strength. Additional information is also given regarding measurement of tensile properties and stress-strain in torsion. An interesting unit is described—a nitrogen gas thermostat operated by the evaporation of liquid nitrogen at a rate of 3–5 l h^{-1} and capable of operating from $-185°$ to $+300°C$. The gas can be cooled or heated at a maximum rate of about 50°C min^{-1}, with a long term stability of $\pm 0.1°C$ and an absolute error of $\pm 1°C$. Such a thermostat would be useful in other applications in thermal analysis. Some 40 materials most of which were synthetic polymers were studied such as various rigid PVC, PET and epoxy, almost all of which were commercial samples. However, some unusual choices were made such as cheese, shellac and bitumen, and some non-polymeric materials namely, lead, tin and Wood's metal.

It is probably best to summarise the main conclusions of the work. The first point is that the temperature range in which aging occurs is generally restricted to a narrow temperature range between T_g (the glass transition temperature) and T_β (the first, i.e. highest) secondary transition temperature. It is considered that from a practical aspect the aging time is very important. Aging is shown to be a basic feature of the glassy state whether polymeric, monomeric, organic or inorganic. It is also shown that aging proceeds in a similar manner for all glassy materials. The

detailed experiments reported in the book show that in the aging range, the time dependence of the small-strain mechanical properties of a glassy material is independent of the specific chemical structure of the material. Thus the behaviour of PVC is largely determined not by its chemical composition but by the fact that it is in the glassy state. Aging is explained in this study from the free-volume concept, that is the idea that transport mobility of particles in a closely packed system is predominantly controlled by the degree of packing of the system (or the inverse measure, the free volume).

This is a detailed study, with meticulous reporting of experiments. The book will be of interest to those who work in the field of polymers and deal with aging phenomena.

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