THE UNIVERSITY OF ADELAIDE

PHYSICAL AGEING
AND
DIMENSIONAL CHANGES
OF ACRYLATE POLYMERS

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PHYSICAL AGEING AND DIMENSIONAL CHANGES OF ACRYLATE POLYMERS

A novel technique for investigating the nature and structure of glassy acrylic polymers, in particular poly(methyl methacrylate) (PMMA), has been developed by studying the dimensional changes of these polymers using a thermomechanical analyser (TMA).

Physical ageing describes a complex process in which an amorphous material in a non-equilibrium state undergoes spontaneous and gradual changes in properties (e.g. decrease in specific volume, increase in creep retardation times, reduction in internal energy, etc.) towards attaining an equilibrium structure. In this work, physical ageing is characterised by length contraction in the glass transition region. The contraction is associated with the collapse of free volume, which is a hypothetical concept used to explain the observed changes during physical ageing. These contractions deviate from the idealised volume-temperature curves which portray T_g as the intersection of the extrapolated liquid and glass lines. The magnitude of length contraction provided a quantitative measure of free volume fraction (f), in which values of f for quenched polymers were found to range from 0.08 to 0.26, but decreased to 0.05-0.06 for slow-cooled PMMA. In addition, free volume fraction was also found to be affected by changes in molecular weight, plasticisation, side-group and main-chain substituents and crosslinking. These variations in free volume fraction leads to the conclusion that a single, "universal" value, as proposed by the Simha-Boyer and Williams-Landel-Ferry theories, is unlikely.

This thesis also investigates of the effects of molecular orientation and residual stresses on the dimensional changes of PMMA. A preliminary study on the dimensional instability of hydrated poly(2-hydroxyethyl methacrylate) (PHEMA) is also presented, in which length measurements may represent a potentially useful tool in elucidating the distribution of water in PHEMA.