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Account / Revue

Polymer ageing: physics, chemistry or engineering? Time to reflect

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Abstract

Polymer ageing may involve *physical ageing* without chemical reaction occurring; *chemical* changes such as crosslinking during curing of a thermoset; *thermal* conditioning at elevated temperature; *photochemical ageing*, as occurs in weathering. This review concentrates on examples involving a combination of two or more of these effects, and with the consequential changes in engineering properties. Events on the molecular level lead to change in the morphology and macroscopic physical properties. For example, in a semi-crystalline polymer, chain scission caused by photo-oxidation, may lead to secondary crystallisation ('chemi-crystallisation'), increasing density, and causing an increase in Young's modulus and reducing ductility. Similar effects may be observed in glassy polymers, due to chain scission accelerating physical ageing. Such effects are particularly common when rapid cooling during moulding has left the polymer in a state far from equilibrium. A common symptom is a change in the residual stress distribution in polymer mouldings and this is discussed. ***To cite this article: J.R. White, C. R. Chimie 9, 2006.***

Keywords: Polymer ageing; Residual stress; Photo-oxidation; Weathering; Chemi-crystallisation; Physical ageing

1. Introduction

'Ageing' is a term used in many branches of polymer science and engineering when the properties of the polymer change over a period of time. The changes may be observed in engineering properties such as strength and toughness; in physical characteristics such as density; or in chemical characteristics such as reactivity towards aggressive chemicals. The origins of the changes may be independent of the surrounding environment and may be chemical, as in the case of the progressive cure of a thermosetting material, or physical, as in the case of a rapidly cooled polymer undergoing volumetric relaxation. In other cases the changes may be the result of interaction with the environment, such as when oxidation leads to chain scission. Sometimes a number of age-related phenomena operate simultaneously and/or interactively. The various kinds of ageing will be defined and discussed here and particular attention will be paid to interactive aspects.

The subject of ageing in polymers is vast and a comprehensive review would demand the collaboration of a large team of experts and would occupy several volumes. This paper presents a personal view and is based largely on studies conducted by the author and his co-workers. The major sections deal with Physical Ageing, Curing, Thermal Ageing and Weathering. These titles are chosen for convenience and some topics do not fall fully under a single heading.

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2. Physical ageing

Physical ageing is probably the most common form of ageing. It often occurs alongside the other forms of ageing described below, and for that reason it is appropriate to deal with it first. Physical ageing occurs when a polymer is in a non-equilibrium state and is caused by molecular relaxations that are biased in the direction required to drive the material closer to equilibrium. This phenomenon is very common and is encountered in thermoplastics mouldings that have been cooled rapidly from an elevated temperature during the shaping operation. The material, in the form of a hot melt, is processed by passing it through a die (extrusion) or into a closed mould (injection moulding, blow moulding). After shaping, the material is cooled rapidly. In the case of amorphous polymers, the material is still cooling rapidly when the temperature drops below the glass transition temperature, T_g. Once below T_g the rate of molecular relaxation is too slow to keep pace with the changes required if the material is to remain at thermodynamic equilibrium. As a result, when the material reaches thermal equilibrium with the surroundings it is not at thermodynamic equilibrium. One symptom of this is the density of the material, because its volume is characteristic of a higher temperature. Consequently, after reaching thermal equilibrium with the surroundings, it will undergo volumetric relaxation, gradually increasing density during an extended ageing period. An example is given in Fig. 1 that is based on data obtained for injection moulded polystyrene by Iacopi and White [1]. Samples were taken, respectively, from the skin and the core of the moulded bar. The thermomechanical history of the two regions is quite different and this accounts for the difference in the density after the moulding operation is complete. Thereafter, the samples of material from the two locations appear to increase in density at fairly similar rates (Fig. 1). The rate of densification will depend on the departure from equilibrium at the ageing temperature, T_a, and on the difference between T_a and T_g. Ageing may be quite rapid at first if T_a is not too far below T_g but the approach to equilibrium will slow down and ageing effects may sometimes still be apparent after many years. If T_a is far below T_g the thermodynamic driving force will be large because the property (e.g. density) will be far from the thermodynamic equilibrium value and will favour change but the kinetics are determined by the difference between T_a and T_g, and this will limit the rate of change.

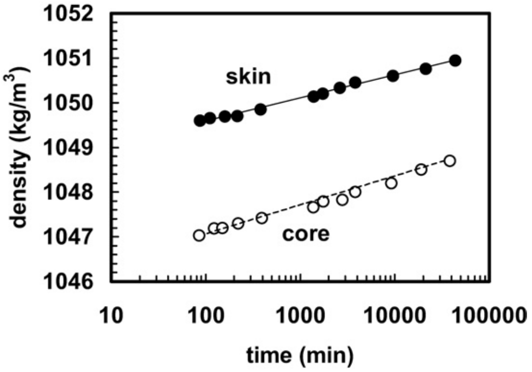

Fig. 1. Density versus ageing time at room temperature of samples extracted, respectively, from the skin and the core of an injection moulded polystyrene bar. Ageing took place in a density column at 23 °C. Further experimental details and discussion of the interpretation of the data are given in Ref. [1].

Ageing of amorphous materials was studied extensively by Struik [2], and his book, published more than a quarter of a century ago, remains the foremost reference on physical ageing of polymers. The book is based largely on experimental data gathered in a meticulous fashion and included examination of the creep behaviour of materials in different states of ageing. Struik's data and his analyses link closely to engineering properties. They also show close connection with the somewhat more fundamental approach to the understanding of the physical principles of polymer ageing followed by many others including Kovacs, Hutchinson, McCrum, McKenna and others [3–12]. Studies of inorganic glasses helped to set the agenda for the studies of these relaxation phenomena in the 1970s [13–15].

2.1. Relaxation behaviour and mathematical description of relaxation behaviour

Struik found that his creep data for amorphous polymers, obtained from tests on similar samples but commenced after various different ageing times, could be superimposed by applying a shift parallel to the time axis (where "time" was measured from the instant that the creep load was applied). A further discovery was that the relaxation behaviour of the polymers that he studied, specifically the onset of the glass–rubber transition, fitted a stretched exponential originally published by Kohlrausch and used also by Williams and Watt [16] ('KWW function') [2]:

$$J(t) = J_0 \exp[(t/t_0)^m] \tag{1}$$

$J(t)$ is the creep compliance at time t; J_0 is its value at $t = 0$; t_0 is a characteristic time that depends on tem-