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Test Method

Indentation testing of polystyrene through the glass transition

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Abstract

The determination of the thermomechanical properties of polymers is vitally important in their characterization. Indentation methods are especially attractive for polymer coatings, since the coatings do not need to be removed from the substrate. In this study, bulk polystyrene has been analysed by conventional cantilever testing and by spherical indentation at different temperatures. It was found that reasonable estimates of the glassy modulus, rubbery modulus and glass transition temperature could be obtained from simple load/unload indentation.

Keywords: Glass transition; Storage modulus; Loss modulus; Indentation; Polystyrene

1. Introduction

Indentation testing of polymers is an increasingly popular area of study because of the potential to apply the technique to polymer films and polymer composites where monolithic mechanical testing is not always feasible. In the case of polymer coatings (paints, lacquers, inks and others) the coating-substrate adhesion is sometimes so strong that it is not possible to remove sizeable amounts of the coating for traditional tensile testing. Some techniques are available to assist in the removal of the coating, such as the use of release agents applied to the substrate, or the chemical dissolution of the substrate. All such methods, however, have the possibility of inducing unknown changes to the polymer coating properties. It is, therefore, preferable to be able to conduct in situ testing of the coating to obtain similar mechanical property information as in the tensile test [1].

Of particular interest in the characterization of thermosetting paint coatings are the thermo-mechanical properties such as the glassy state modulus, the glass transition temperature and the rubbery state modulus. Most coatings are used in the glassy state (below T_g) to ensure good scratch resistance and other important properties. For these reasons it is important to accurately determine the glassy state modulus. The degree of crosslinking that occurs during paint curing is an important control parameter for paint processors. The degree of crosslinking affects the glass transition temperature and the rubbery state modulus. In fact, the modulus in the rubbery state (above T_g) is directly proportional to the crosslink density of thermosetting polymers. Thus, the measurement of the T_g and the modulus above T_g is very useful for characterizing the cure process in thermosetting polymers.

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Although indentation testing has long been applied to metals and ceramics for the accurate determination of modulus and hardness, the application to polymers has been limited to date due to the time-dependent nature of the polymer mechanical behaviour. A schematic diagram showing the typical shape of the loading and unloading curves during indentation testing and the definition of relevant parameters are given in Fig. 1.

A recent attempt to determine the modulus at room temperature of glassy polymers by Nowicki et al. [2] analysed the unloading slope to give the contact stiffness S which can then be related to the reduced modulus E_r

$$E_r = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A}}, \tag{1}$$

where A is the contact area. Most analyses use the method of Oliver and Pharr [3] to determine the contact area from the measured load and penetration depth. The reduced modulus depends upon the elastic modulus (E) and Poisson's ratio (v) of both the indenter (i) and substrate (s):

$$E_r = \left[\frac{(1-v_i)^2}{E_i} + \frac{(1-v_s)^2}{E_s}\right]^{-1}. \tag{2}$$

More accurate determinations of polymer elastic moduli have been obtained using the continuous stiffness measurement system utilizing a small amplitude vibration in addition to the load and unloading process. This technique has been applied to both glassy polymers [4] and rubbers [5–7] with viscoelastic properties determined over a range of oscillation frequencies. Such techniques are able to determine the elastic and storage moduli and the loss tangent for a variety of different materials. In one study, the storage modulus of a glassy polymer was determined at various temperatures below T_g [4].

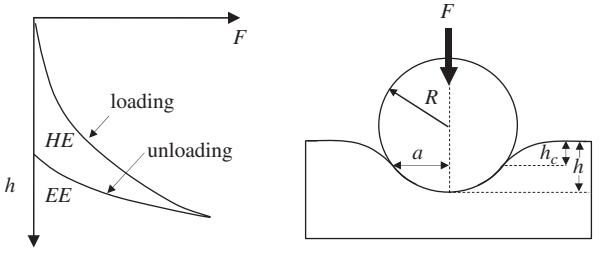

Fig. 1. Schematic loading and unloading curves with illustration of the indentation process.

A simpler method that analyses the load/unload hysteresis has also been proposed for measuring the loss tangent or loss modulus of polymers. Nowicki et al. for example determined the ratio of energy dissipated to energy stored for a number of polymers as a function of the amount of UV irradiation experienced [2]. The decrease in the energy ratio was taken as indicative of a reduction in viscosity and was related to increased cross-linking by the UV radiation. Gilbert et al. [8] considered that the hysteresis energy (HE) was better related to the loss modulus (E'')

$$\mathrm{HE} = \pi\Delta\varepsilon^2 E'' = KE''h_{max}^2, \tag{3}$$

where $\Delta\varepsilon$ is the strain increment, h_{max} is the maximum indentation depth, and K is a geometry dependent constant. Thus, the ratio of the HE to the maximum indentation depth squared is related to the loss modulus, and has been termed the "energy dissipation factor" or EDF

$$\mathrm{EDF} = \frac{\mathrm{HE}}{h_{max}^2}. \tag{4}$$

In the present study, the use of simple load/unload indentation tests at different temperatures has been evaluated for the estimation of thermo-mechanical properties of polystyrene.

2. Materials and experimental methods

The base material used was commercial polystyrene, Austrex 103 granules, supplied by Polystyrene Australia. The polystyrene granuals were heated in a hot press to 165 °C and held with slight pressure for 5 min for melting to occur. Then, a pressure of 20 bar was applied, held and released thrice for densification and degassing. Finally, the polystyrene was held in the same condition for 15 min and cooled to room temp. From the centre of these plates small square platelets were cut to $10 \times 10 \times 3.25$ mm to form test samples.

Indentation measurements were performed on a commercial dynamic mechanical analyser (TA Instruments DMA MODEL Q800). The indenter used was a stainless steel sphere, with a radius of 0.5 mm, glued onto a brass holder. The compliance of the apparatus was less than 0.6 μm N^{-1} which was determined by a prior calibration of DMA in compression mode. A typical indentation procedure started with a position-controlled movement of the indenter towards the sample until the surface is contacted with a pre-load of 50 mN. This procedure