Micro-Indentation Relaxation Measurements in Polymer Thin Films

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A micro-indenter consisting of a piezo-electric driven flat cylindrical punch has been used to measure the dynamic mechanical properties of polystyrene films as thin as 50 μm. The measured viscoelastic response was sensitive to the bonding of the polystyrene to an underlying silicon substrate for films which were thinner than one indenter diameter. The instrument therefore was shown to have practical use in measuring the dynamic mechanical response of polymer films, and the strength of bonding between disparate materials.

Key words: Dynamic mechanical test, microindentation, polymer films, polystyrene, viscoelastic

INTRODUCTION

Polymers are used extensively in many applications in thin film form, for example as free standing films, or as coatings which are next to rigid substrates. In electronic packaging, adherent epoxy underfills can be used to modify the localized stress concentrations which can arise due to differences in coefficients of thermal expansion of the different materials. The mechanical state within the polymer necessarily varies from point to point within the thin film, as can the strength of the adhesion between the polymer and the substrate. The mechanical properties of polymers are relatively strongly dependent on time and temperature, and the standard engineering tests to characterize their "strength" take this into account. Thus stress relaxation, creep and dynamic mechanical relaxation measurements are generally used to compare the relative mechanical performance of polymers. When constant displacement rate tests are used, strain rate dependence of the deformation behavior is usually measured.

In most practical cases, even in thin film applications such as found in electronic packaging examples, the typical dimensions of the polymer component are much larger than the dimensions of individual molecules (randomly coiled molecules occupy approximately spherical spaces of diameters which are typically under 10 nm). At scales much larger than this, the material can be considered a continuum and the usual mechanics can be invoked to model the deformation behavior, and bulk tensile properties (which will vary with resin and processing) can accurately describe the time dependent properties of the thin film. However, in most practical cases, the local mechanical properties within the polymer vary from point to point. This may arise due to microstructural inhomogeneities (for example, topographic variations in the interface), or variations in local constraint (due to local decohesion) from the adherent rigid substrate. These local variations in mechanical properties cannot easily be predicted from bulk property measurements, and it is useful to develop an experimental technique to measure the inhomogeneity. The measured parameters can then be used to predict local failures or to optimize processing to minimize such failures.

There has been considerable interest recently in nano-indentation testing, in which the hardness and modulus of thin films have been measured at ex-
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**Fig. 1. Schematic diagram of microindenter.** (1) piezoelectric driver, (2) furnace, (3) indenter tip, (4) sample, (5) load cell, (6) piezoelectric driver amplifier, (7) current source, and (8) microcomputer.

...extremely small dimensions. These have been mainly on hard materials. The elastic behavior, particularly under spherical and pyramidal indenters, has been modeled extensively. Time dependent creep behavior of soft materials has been studied in detail by Li and co-workers. Microhardness testing, familiar to metallurgists, has been used to measure inhomogeneity of properties in polymers. A typical hardness test involves applying a fixed load to the indenter, and measuring the resultant size of indentation. This has been related empirically to the yield stress of the material, but the test normally has not controlled the strain rate.

This work presents the results from micro-indentation testing of polymer thin films. The indenter diameter is matched to the specimen thickness, since the stress field under the indenter scales with the indenter diameter. The practical usefulness of the dynamic mechanical measurements is demonstrated by showing that the properly normalized experimental data compare closely to measurements from bulk specimens tested in bending. Elastic calculations are used to show that the empirical normalization procedure developed for thick specimens does not hold for thin specimens.

**EXPERIMENTAL**

The specimens used were prepared from atactic polystyrene (with average molecular weight of $3.6 \times 10^5$) which was compression molded to varying thickness ($t$) over the range $50 \mu m < t < 1500 \mu m$, and slow cooled. The sample surfaces were checked to ensure they were smooth and relatively flat and parallel. The material was chosen since the temperature dependence of its viscoelastic properties were well known, with an unambiguous glass transition at about 100°C. It also adhered from the melt to clean silicon surfaces, which made it useful for determining if the technique had potential in detecting decohesion from the substrate. The atactic polystyrene was also prepared using a similar compression molding procedure in bulk form ($5 \times 25 \times 2 \text{ mm}$). This allowed for a quantitative comparison of the standard viscoelastic properties, measured using a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA), with the micro-indenter results. The standard test involved bending in single cantilever beam mode, at a frequency of 2 Hz. The rate of change of temperature was 2.5°C/min.

A schematic diagram of the micro-indenter was as shown in Fig. 1. The indenter was moved by a piezoelectric driver, the position of which was measured by an attached strain gauge. The displacement of the tip was precisely controlled by monitoring the strain gauge output. The measured hysteresis, which has been a major problem with piezoelectric drivers, was therefore kept to a minimum. The indenter itself was made from cold worked steel wire of varying diameters from 150 μm to over 300 μm. These dimensions were purposely kept relatively large to match the specimen thickness. The instrumentation was designed to be used directly with much smaller indenter diameters. The maximum capacity of the load cell was approximately 5 N, and the range used for the viscoelastic measurements was several orders of magnitude smaller. The load cell was therefore a relatively stiff component in the load train, which was an important consideration in attempting to measure accurately the material properties under precise load or displacement control. This distinguished this kind of test from many hardness tests in which the displacement and loading rates were not controllable over set ranges. The indenter tip and specimen were enclosed in a small furnace which was heated by passing a controlled current through a resistive winding. The indenter position and furnace temperature (measured with a strain gauge and thermocouple, respectively) were controlled through a microcomputer. The displacement of the tip and the resultant load, as well as the testing temperature, were recorded with the same microcomputer.

The temperature history of each dynamic mechanical relaxation spectrum measurement was similar to that in a standard instrument (DMTA): the temperature was increased linearly with respect to time at a rate of 2.5°C/min. The temperature of the specimen lagged the furnace temperature, due to the finite heat transfer rate to the polymer, so the temperature was fixed by normalizing to the observed glass transition. The glass transition temperature was measured on a bulk compression molded sample with the standard dynamic mechanical thermal analyzer. The same material was then tested in the microindenter and the transition temperatures were...