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The dynamic mechanical analysis of hydrogel elastomers [1]

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Abstract

An internal liquid bath which can be fitted into the furnace of a Perkin-Elmer DMA-7 has been developed. This new internal liquid bath allows the samples to be tested by dynamic mechanical analysis (DMA) in a liquid medium, not only under isothermal condition but also in the temperature scan mode. It overcomes problems such as sample dehydration when using DMA for hydrogel materials and soft tissues and is superior to the external liquid bath which is normally difficult to run in the temperature scan mode. A plot of program temperature versus sensor temperature, demonstrates that introducing the extra mass of the liquid bath and the liquid medium does not interfere the system when operating in the temperature scan mode. DMA equipped with this new liquid bath has been used in studying poly(vinyl alcohol) (PVA) hydrogel samples; the results are discussed.

INTRODUCTION

Since the discovery of the remarkable biomedical properties of poly(2-hydroxyethyl methacrylate) by Wichterle and Lim in 1960 [1], a wide range of hydrogel materials have been examined as potential candidates for replacement of soft tissue and for other biomedical applications. Needless to say, the mechanical properties of the hydrogel material are usually an important criterion in material selection for its biomedical application. The mechanical properties of a hydrogel are dependent on its water content and will change when it is not in contact with liquid or not in a high humidity environment due to dehydration. Thus it is generally necessary to test the material either in a water bath or in a high humidity environment.

Modern DMA analyzers have become very versatile and sensitive instruments, and perhaps show the greatest potential of all the family of thermo-analytical instruments. It has been widely used to measure the structural and intrinsic property changes from very soft, rubber-like, to

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very rigid, metal-like, materials. However, reports on using DMA to analyze hydrogel materials and soft tissues are still rare, largely because the DMAs available on the market are not equipped with a water bath. Attempts have been made by several groups to use an external liquid bath in order to perform dynamic mechanical experiments in fluid environments [2, 3]. However, the external bath is mostly suitable for an isothermal study because it is difficult to program the temperature of the fluid bath and to achieve temperature uniformity.

In order to meet the increasing needs to characterize hydrogel materials and to bring the DMA technique into the biomedical field, we have developed an internal liquid bath which can easily fit into the furnace of a Perkin-Elmer DMA-7 analyzer. Because this bath has a relatively small mass, no extra heater is needed to program the temperature. This set-up has been used to study the viscoelastic properties of some PVA hydrogels in the temperature scan mode.

EXPERIMENTAL

Bath design

The Perkin-Elmer DMA-7 has a vertical set-up which makes it easier to build an internal liquid bath than with the horizontal set-up. The 1.75 mm gap between the furnace wall, with inside diameter of 29 mm, and the fixture, with outside diameter of 25.5 mm, leaves space for insertion of an internal liquid bath. The bath is made of a stainless steel cup 51 mm high, 29 mm outside diameter, and 0.9 mm wall thickness. In order to achieve good contact between the furnace and the bath cup, the outside diameter of the cup is very close to the inside diameter of the furnace. Two small grooves were cut on the outer surface of the cup to facilitate insertion and removal of the cup from the furnace. On the bottom of the cup, another groove was cut to fit the projection on the furnace from the thermal wire. A schematic diagram of the DMA with an internal bath is illustrated in Fig. 1.

Temperature check

A temperature check run was conducted, heating from 4 to 90°C at 2°C min^{-1} with the bath filled with 12 ml of deionized water which is sufficient to immerse both the sample and the thermocouple in the parallel plate fixture.

Materials

PVA hydrogels were prepared by first dissolving PVA powder in a mixed solvent of dimethyl sulfoxide (DMSO) and water at elevated temperatures and then cooling down to −17°C overnight. The molded films were then

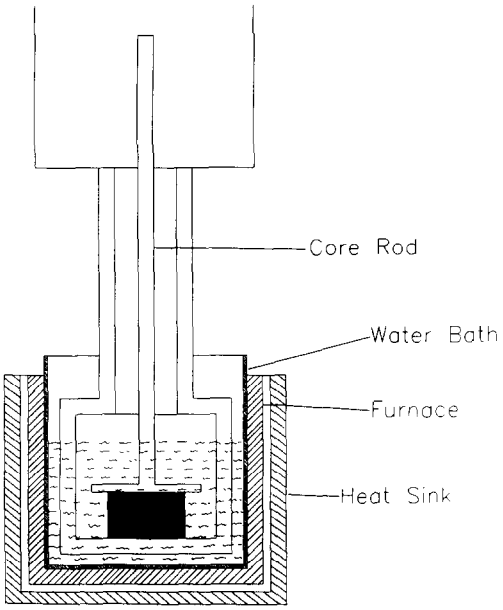

Fig. 1. Schematic diagram of the DMA with an internal water bath.

cleaned with water until no DMSO residue was left in the gel. The film (≈2.5 mm thick) was then cut into discs 5 mm in diameter for DMA measurements.

Equipment

A Perkin-Elmer DMA-7 with a parallel plate fixture was used for all the DMA measurements. To prevent the hydrogel disk from moving during the test, a 600 grit sand paper was adhered to the bottom plate. Typically, 12 ml of deionized water was used to immerse the hydrogel disc.

Temperature scan mode

A dynamic stress at 1 Hz coupled with a static stress was applied to cause about 1% strain on the disc. The temperature was scanned from 20 to 55°C at 2°C min^{-1}.

Creep-recovery mode

Two tests were conducted in this mode. One was to obtain the stress versus strain curve similar to the one obtained from an Instron, by applying stress at a constant rate until a designated strain. The temperature was kept constant. The other test was to apply an instantaneous stress to give about

10% strain and hold at that stress for 15 min, and then remove the stress instantaneously for recovery.

RESULTS AND DISCUSSIONS

Because the water bath introduced an extra mass of water and the cup into the testing environment, it has to be confirmed that the bath itself and the liquid used does not interfere in conducting the heat from the furnace to the test sample, and that the furnace has enough energy to heat the system in the temperature mode. A calibration check run, was therefore conducted in which the system was heated from 4 to 90°C at 2°C min^{-1}. As shown in Fig. 2, the actual temperature overlaps almost exactly with the programmed temperature without much lagging. This result is expected because in this internal bath the added mass is relatively small (the stainless steel bath has a weight of 42.6 g). Unlike the external bath, which is larger, no turbulence is needed for this bath to achieve temperature uniformity. In fact, the uniformity with the water bath should be better than without the bath because the thermal conductivity of stainless steel and water is better than that of air.

Thermal stability is one of the important characteristics in selecting hydrogen materials for biomedical application. In most applications, it is required that the hydrogel should be thermally stable at least to body temperature, 37°C. Also, in most cases it is undesirable that the material has any significant change in mechanical property due to structural and

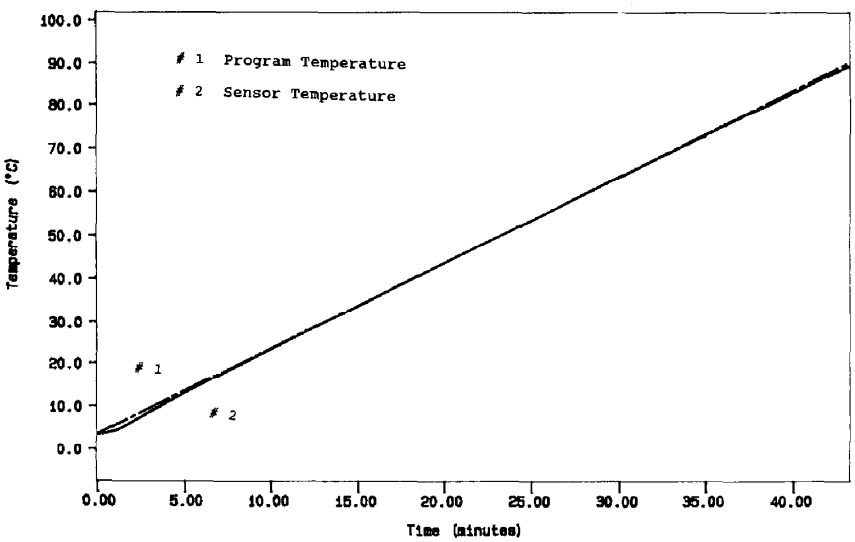

Fig. 2. Temperature calibration curve with water bath.

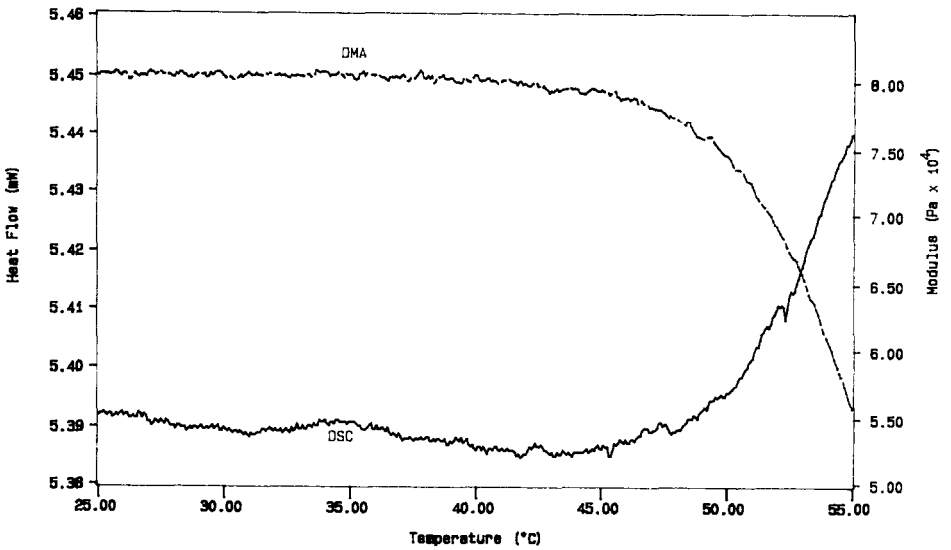

Fig. 3. DMA and DSC plots of a PVA hydrogel.

intrinsic changes around 37°C. Because DMA can be used to measure mechanical properties directly and their variation with temperature, it is obvious that it could become a useful tool in material characterization for the biomedical industry. Various PVA hydrogels of different water content from 70% to 90% were tested in the temperature scan mode. It was found that all these PVA hydrogels have a similar pattern in the modulus versus temperature plot, the modulus being almost constant up to about 45–47°C, then decreasing after that, although their initial moduli are different. Figure 3 shows one example of these plots. These results indicate that all these PVA hydrogels, regardless of their water content, have no structural changes and are thermally stable at least up to 45°C. After 45°C, the modulus starts to decrease which suggests some structural change in the PVA hydrogel. This structural change was also observed in the differential scanning calorimetry (DSC) measurement. The endothermic peak with onset temperature of around 47°C was attributed to the disentanglement of the flexible molar chains of the PVA polymer [4]. When we plot the DSC and DMA curves together, the two methods reveal the structural change at almost the same temperature (Fig. 3). This study indicates that the PVA hydrogel has the thermal stability for application as an implant material.

DMA equipped with the water bath can also be used for biomechanical property testing of various hydrogel materials and soft tissues which would otherwise be tested by an Instron. Because samples for biomedical application are normally very small and usually require a small load cell, DMA can replace Instron, and offers a better result. For example, we used DMA for the compression test of PVA hydrogels in creep mode which

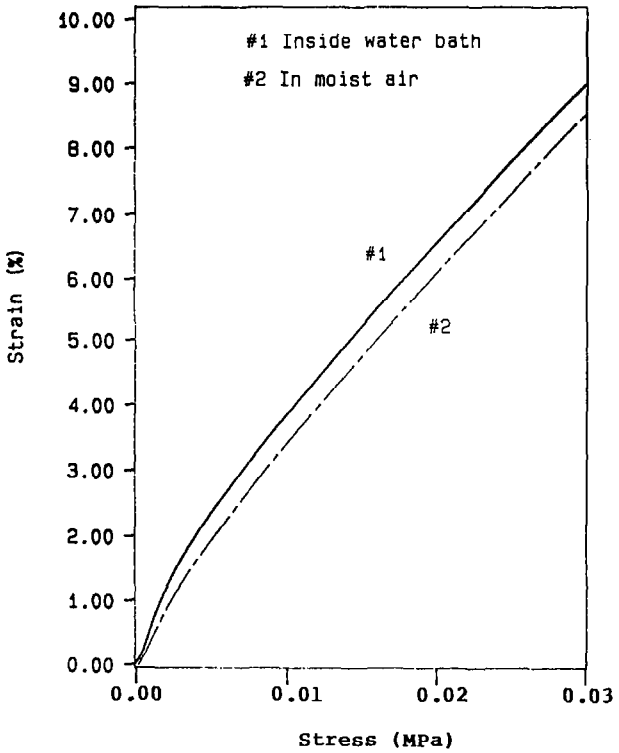

Fig. 4. Stress vs. strain plot of a PVA hydrogel with and without sample being immersed.

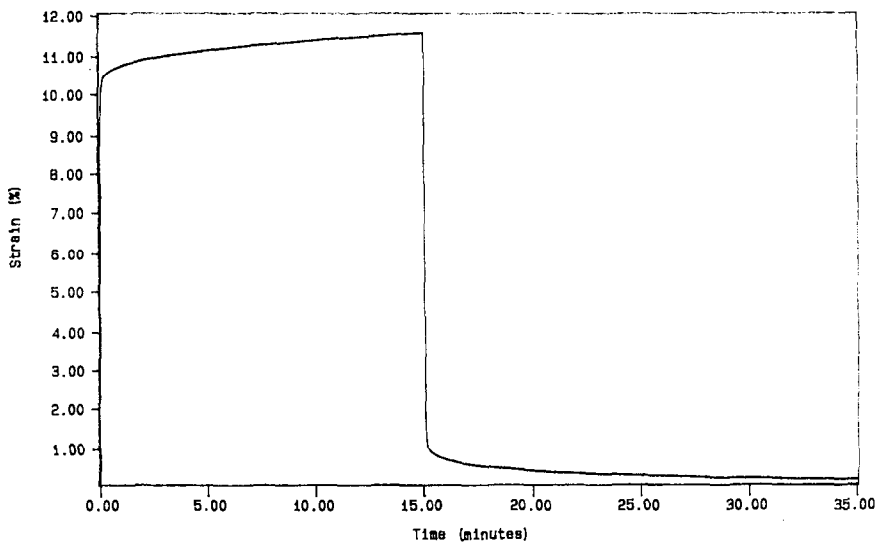

Fig. 5. Creep-recovery curve of a PVA hydrogel.

provided us with a stress versus strain curve (Fig. 4). Tensile tests can also be conducted with a different fixture. Calibration, however, might be needed when the sample is immersed in liquid if absolute mechanical data are important, because it has been reported that the mechanical properties could be different in a liquid environment due to buoyance from the liquid medium and the effect of fluid drag. We have found that in dynamic loading, the storage modulus of a PVA hydrogen is 7.7% less when immersed in water than when not immersed. In static loading, the modulus difference between immersed and not immersed is about 5.5% (Fig. 4).

The creep-recovery test is normally used to measure the material's viscoelastic property which is often an important characteristic for hydrogel materials in biomedical applications. An example of a creep-recovery test of PVA hydrogel is shown in Fig. 5.

CONCLUSIONS

The new small-mass internal liquid bath developed by us is a simple cost-efficient device which allows DMA testing in liquid environments at varying temperatures. DMA equipped with this internal liquid bath can be a useful technique for the biomedical industry in characterizing both synthetic hydrogel materials and various soft tissues. This liquid bath can also be used for testing other samples in a liquid medium with DMA.

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