

OXIDATIVE AND HYDROLYTIC STABILITY STUDIES ON MEDICAL THERMOPLASTIC URETHANES

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Abstract

Thermoplastics urethanes (TPU) are widely used in medical devices due to their broad property range, processing flexibility, and biocompatibility. Increasingly, these devices are subjected to longer duration use, and exposed to a wide variety of chemically active agents. We conducted a preliminary investigation on method suitability for oxidative and hydrolytic stabilities on model TPUs and some TPU catheters. Techniques used include oxidative induction time (OIT) by differential scanning calorimeter (DSC), pressure DSC, and melt rheology. It was found that due to TPUs' chemical structure, distinct OIT onsets were difficult to obtain. However, melt rheology was capable of quantifying the alcohol hydrolytic molecular weight degradation process.

Introduction

Due to their broad property range, processing flexibility, and biocompatibility, thermoplastics urethanes (TPU) are widely used in medical devices. Increasingly, these devices are subjected to longer duration use, and exposed to a wide variety of chemically active agents. Therefore, a full understanding of all degradation pathways is critical for device performance. To this end, we initiated a preliminary study aimed at evaluating various techniques for polymer degradation. During oxidative degradation, a single initiation event forms peroxides and hydro-peroxides which can propagate and lead to many degraded polymer chains, as depicted in Figure 1.

The OIT test with a differential scanning calorimeter (DSC) is widely used for polyolefin stability studies, and it has found utility in many other polymer systems[1-7]. Although not specific to the antioxidant package, OIT provides a measure of the relative total thermal stability of the polymer system, and is therefore a very attractive technique for evaluation. In addition, it is expected that molecular weight degradation occurs during contacts with active disinfectant chemicals such as ethanol water solutions. It will thus be desirable to have a molecular weight based technique to monitor the degradation.

Experimental

To assess the oxidative stability of TPUs, several commercial catheter tubing segments were subjected to

oxidative induction time (OIT) measurements on a differential scanning calorimeter (DSC) according to ASTM 3895[8], where the sample is rapidly raised to a preset temperature and held isothermally with an oxidizing gas flow while the onset of autocatalytic oxidation is measured. For this measurement, a DuPont (TA Instruments) 910 DSC cell and cell base was used, with air flow of 100ml min⁻¹ as the oxidizing medium. In addition, a pressure DSC experiment was also conducted in the constant volume mode, using oxygen pressures from 1.0 MPa (150 psi) to 2.8 MPa (400psi).

To evaluate possible molecular weight degradations upon exposure to common disinfectant chemicals, melt rheology was applied using the well established relationship for linear polymers [9-10],

$$\eta = K Mw^{3.4} \quad (1)$$

Where η is the steady shear limiting viscosity
 Mw is the weight average molecular weight

For simulated disinfectant exposure, ethyl alcohol was used at various strengths and immersion times. After alcohol immersion, prior to melt rheology determination, samples were rigorously dried in a vacuum oven at 60°C under continuous 95 KPa (25 in Hg) vacuum. Melt rheometry was conducted with a Rheometrics RDS II instrument in the parallel plate geometry with the frequency sweep mode from 0.1 to 300 rad sec⁻¹. Various temperatures were used but most data were collected at 180°C to minimize sample degradation during the melt experiment.

Samples used in this study included a commercial medical grade aromatic polyether TPU with 85 Shore A hardness as the model compound. In addition, several commercial catheters utilizing different thermoplastic urethanes were studied.

Result and Discussions

Thermal Analysis

A typical OIT scan for a polyurethane catheter segment at 220°C is presented in Figure 2.

Surprisingly, even at this elevated temperature, little thermal activity was evident with thermal detection. Thus

a pressure DSC experiment was attempted, first at about 1.0MPa (150psi) at 180°C, and later at 2.8 MPa (400psi) oxygen pressure (Figure 3; again, no distinct thermal event was detected.

Although signs of oxidative degradation were plainly evident--samples turned dark yellow to brown--little expected thermal activity (exothermic) was seen. This may be attributed to the inherent fire-retardant nature of polyurethanes. There is also the possibility that the exothermic oxidation reactions were nearly balanced by the endothermic chain-scission reactions.

Melt Rheology

Due to the well known moisture sensitivity of polyurethanes, prior to melt processing (compression molding for sample preparation) and melt rheology, samples were rigorously vacuum dried to within 0.03% of constant weight, according to manufacturers recommendations [11]. A typical drying curve after ethanol exposure is shown in Figure 4. It is evident from the data that careful attention to drying is critical for melt processing. From the magnified scale, near constant weight was not achieved until nearly 80 hours of vacuum drying at 60°C. Still higher temperatures were avoided for drying to minimize the possibility that re-condensation reactions would reverse the reduced molecular weight after hydrolysis.

For the model commercial medical grade polyurethane, the sample melt viscosities were measured against immersion time (presented in Figure 5).

During the accelerated disinfectant immersion, it was noted that after 2 days (50 hours), the loss of antioxidants during the immersion might contribute to the more erratic data measured, and a common antioxidant Irganox 1076 [12] at the 0.25wt% level was added to the immersion medium. In addition, at each time period (over 10 days of experimental time), a control sample was determined as an added consistency check. Early data points in Figure 5 clearly indicated thermal molecular weight degradation during melt rheology determinations, and thus the first two data points were repeated, presented in Figure 6. Clearly, a time-dependent reduction in molecular weight-controlled viscosity was evident under these accelerated conditions. The initial rate of melt viscosity reduction is a kinetic parameter useful for further analysis.

Conclusion

To evaluate methods for thermal oxidative and hydrolytic stability of medical TPUs, a preliminary study was conducted using thermal analysis and rheological techniques. It was determined that traditional thermal methods for polymer oxidative stability, the OIT test,

conducted either with a standard DSC or a pressure cell under elevated oxygen pressures, did not produce a distinct onset suitable for further analysis. At the mean time, a melt rheology method including careful control of detail procedures and immersion media produced very promising results. Since rheology data is based on molecular weight, the rheology method could provide meaningful property assessment and predictions for TPUs contacting hydrolytic medium for significant indwelling times and at elevated (body) temperatures, pending further development and correlation with mechanical testing data., As the experiments are currently ongoing, additional data will be presented as they become available.

References

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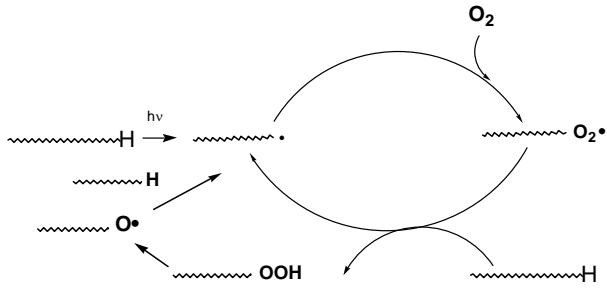


Fig.1, Schematic polymer oxidative degradation pathway

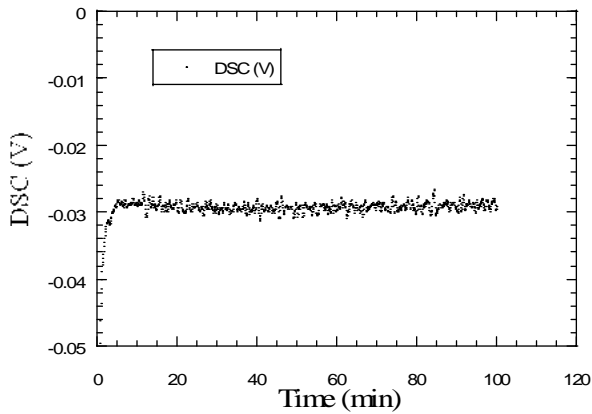


Figure 2, TPU catheter segment 220°C OIT

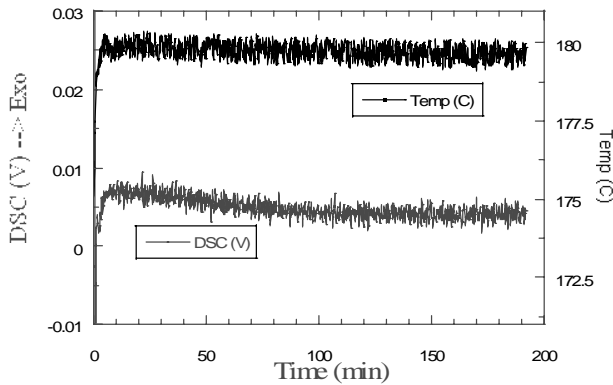


Figure 3, TPU catheter segment PDSC 1 MPa oxygen OIT

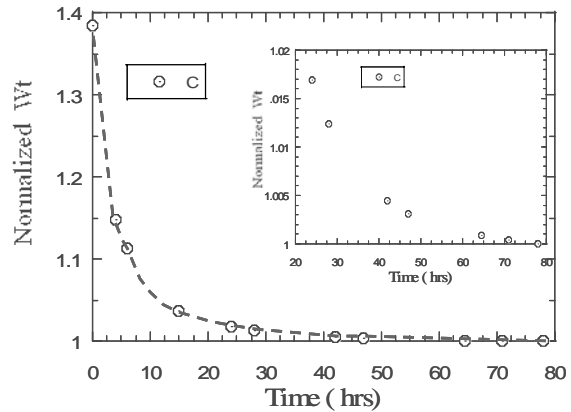


Figure 4, Post exposure drying, inset at expanded scale

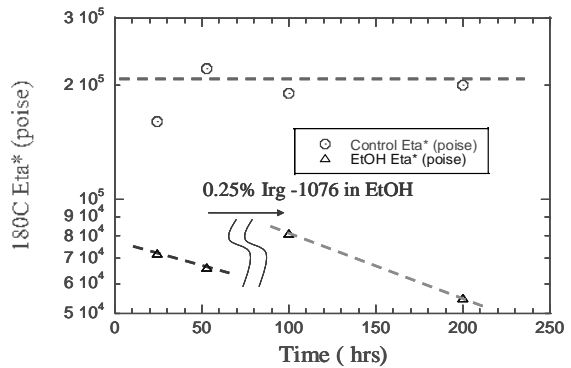


Figure 5, Model TPU rheology after accelerated hydrolytic ethanol immersion

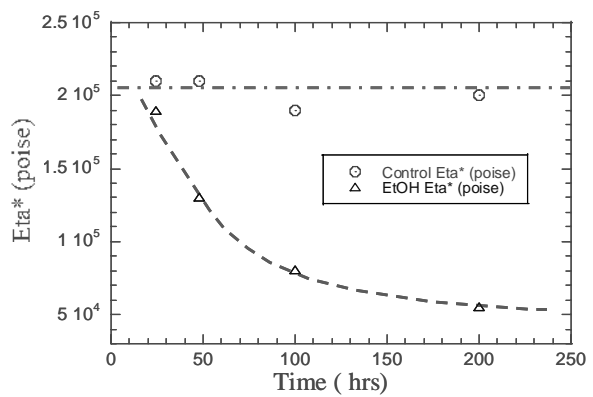


Figure 6, Revised melt rheology data with antioxidant addition.

Key Words: TPU, OIT, Hydrolytic Degradation, Disinfectant, Rheology