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Definition of test parameters for dynamic mechanical testing of polymeric implant materials

Abstract: The selection of appropriate test conditions is of critical importance in mechanical testing of biomaterials. In particular the definition of dynamic test conditions is requiring high efforts. In this work, a thermoplastic semi-crystalline polymer was characterized regarding mechanical properties by dynamic mechanical analysis (DMA). Time-temperature-superposition (TTS) of dynamic mechanical data provides an efficient method for the experimental design of follow-up studies. Our focus was to provide test conditions for cyclic tests, which correspond to viscoelastic materials. The results show, that the test temperature for dynamic mechanical fatigue tests, as an indicator of mechanical modification for viscoelastic materials, should necessarily remain below the onset temperatures of storage modulus and loss modulus. Moreover, changes in material characteristics due to varying frequencies should be considered when constructing a master curve for the evaluation of test frequencies. Therefore, TTS is particularly beneficial for the rapid determination of test parameters for accelerated material examination.

Keywords: dynamic mechanical analysis, time-temperature-superposition, polymer characterization, fatigue test, biomedical applications

<https://doi.org/10.1515/cdbme-2021-2174>

1 Introduction

In biomedical engineering, new applications and requirements have led to a focus on polymers over the last decade. With the further development and new composition of polymer materials, the methodology for their

characterization requires ongoing improvement, as well.

Due to the structural composition of polymers, their properties (e.g. mechanical or thermal) are time-dependent and can be characterized by DMA or dynamic mechanical thermal analysis (DMTA).

Therefore, a specimen is exposed to a periodic oscillating load with fixed frequency and amplitude while temperature is ramping up in defined matter. The investigation of wide frequency ranges is possible in a reasonably short period of time and viscoelastic properties can be evaluated by forced oscillations and the resulting phase shift between stress and strain. Test frequencies have to be below the natural frequency of the specimen, typically in the range between 10^{-2} - 10^2 Hz.

In order to use the data of DMA for the definition of test parameters for fatigue tests, especially wide frequency ranges and wide temperature ranges have to be investigated. Therefore, a combination of different parameters during one test is appropriate. Multifrequency temperature sweeps include frequency sweeps at constant temperatures, as well as an incremental heating over time.

The determination of these relationships can be evaluated in a simplified way by the TTS and test parameters can be estimated. According to theory, this principle uses the equivalence of time and temperature to reduce test times and cover an extended frequency range. In particular, this has been shown for thermo-rheological simple polymers, especially single-phase, single transition and amorphous polymers with linear viscoelastic properties [1]. However, other studies show that the application can be transferred to crosslinked, crystalline and especially nonlinear viscoelastic polymers [2-4].

In order to generate master curves the empirical Williams-Landel-Ferry (WLF) equation is used. Basis of this equation is the assumption of linear increase of fractional free volume of polymers with increasing temperature [2, 3].

The isothermal frequency sweeps are shifted following WLF equation and therefore examined shift factors for x- and y-direction. This procedure is shown schematically in Figure 1.

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Figure 1: Schematic illustration of curve shifting experimentally determined isothermal frequency sweeps (left) for construction of a master curve in an extended frequency region (right); arrows indicate both horizontal and vertical shift

The isothermal experiments for the exemplary measuring range of 10^{-1} - 10^2 Hz are shown in black. The resulting master curve was constructed by shifting these curves horizontally and vertically.

2 Materials and Methods

2.1 Sample preparation

Semi-crystalline poly(L-lactide) PLLA (RESOMER L210, Evonik, Germany) was chosen as a model material due to its various applications in biomedical engineering. Solution cast films were prepared by dissolving PLLA in chloroform followed by a dipping procedure.

Specimens for dynamic mechanical analysis were lasercut in $2 \times 20 \text{ mm}^2$ rectangular shape by using Trotec Speedy 300 lasercutter (Trotec Laser GmbH, Germany). The average thickness of tested films was $210 \mu\text{m}$.

2.2 Dynamic mechanical analysis

DMA was performed using the DMA850 test bench from TA Instruments (TA Instruments Inc., USA). For examining dynamic mechanical properties, tension-test setup was chosen and 6 rectangular shaped specimens were uniaxially deformed. Specimens were clamped with 5 mm clamping length. Examined temperature range was 0 - 120°C with 2°C temperature increments and an equilibration time of 2 minutes for each increment. Furthermore, frequency sweeps were performed at each temperature step in logarithmic increments between 0.1 - 100 Hz. The oscillation

amplitude was $2 \mu\text{m}$ to ensure that the measurement was carried out

with low forces and low strain, according to the literature [5]. Preconditioning was set to 0.1 N . Additionally, the Force-Track-Function of TRIOS Software (TA Instruments Inc., USA) was activated to optimize static force depending on dynamic force and prevent from overstraining the specimens.

Evaluation of experimental data was performed with respect to relevant parameters storage modulus E' , loss modulus E'' and damping factor $\tan\delta$.

2.3 Time-Temperature- Superposition

By applying TTS on experimental data sets, master curves for the corresponding characteristic parameters as a function of frequency can be generated. These master curves were prepared using TRIOS software. Three different reference temperatures were selected and the corresponding curves were compared. Besides a reference temperature of 37°C , which represents human body temperature and is therefore often the operating temperature of implants, master curves for reference temperatures just below glass transition T_g and right within T_g were compared. Master curves for different reference temperatures allow the evaluation of various thermal states of the polymer and consequently the determination of an appropriate testing temperature.

Furthermore, master curves for storage and loss modulus as well as for damping factor were generated by evaluating 61 frequency sweeps from DMA studies over the defined temperature range. The curve shifting was performed based on temperature data only, shifting in both the x- and y-direction. The calculation was performed on the basis of the WLF equation in order to obtain the most reliable results possible, even in the T_g range.

3 Results and Discussion

3.1 Dynamic mechanical analysis

The multifrequency temperature sweeps were first analyzed as typical DMA plots at fixed frequencies. Temperature sweeps were examined throughout the temperature range from 0-120 °C for 1, 10 and 100 Hz separately. Additionally, to provide appropriate plots, averaged curves instead of 6 individual measurements are shown in Figure 2.

Figure 2: Results of multifrequency temperature sweeps of PLLA samples for fixed frequencies of 1, 10 and 100 Hz

The material shows distinct viscoelastic properties. With increasing frequency, the onset temperatures of storage and loss modulus, as well as signal peak of $\tan \delta$, drift to higher temperatures due to occurring molecular chain rearrangement processes.

When comparing the curves for each frequency, storage and loss module do not exhibit any conspicuous slope variations. In contrast, the damping factor $\tan \delta$ shows a significant change at 100 Hz. In particular, the peak, and thus the maximum amplitude, is rather high in comparison to other investigated frequencies. According to the calculation of $\tan \delta$, curves increase is due to convergence of curves for storage and loss module at the end of glass transition region. The high test frequency causes a drop in storage modulus and an increase or larger plateau in loss modulus, simultaneously. It has been reported that DMA curves of PLLA occasionally show an increase in storage modulus after glass transition region, which is due to cold crystallization [6]. However, this effect has not been observed.

Corresponding parameters of plotted measurements are summarized in Table 1.

Table 1: Temperatures derived from DMA data to evaluate viscoelastic properties of PLLA samples

frequency	onset E' [°C]	onset E'' [°C]	peak tan δ [°C]
1 Hz	56.3	51.2	77.0
10 Hz	61.8	54.8	81.0
100 Hz	64.6	56.1	88.0

Storage modulus increases from 56.3 °C at 1 Hz to 61.8 °C at 10 Hz and 64.6 °C at 100 Hz test frequency. Similarly, the onset temperature of loss modulus increases from 51.2 °C to 54.8 °C and 56.1 °C, respectively. Furthermore, the peak of $\tan \delta$ drifts from 77 °C at 1 Hz to 81 °C at 10 Hz and 88 °C at a 100 Hz.

3.2 Time-Temperature-Superposition

The master curves generated by applying TTS-Principle on experimental data were evaluated for three different reference temperatures. Figure 3 shows exemplary results of TTS for a single specimen at three different temperatures.

Figure 3: Exemplary illustration of master curves for storage modulus and damping factor of PLLA samples at different reference temperatures (37 °C, 50 °C and 75 °C)

As shown in Figure 3, master curves for 37 °C and 50 °C are almost identical, indicating that mechanical properties are likewise the same for both temperatures. In contrast, the curve for 75 °C reference temperature is shifted for 10

decades in x-direction. This shift is equally significant for storage modulus and $\tan\delta$. Typical test frequencies for the intended cyclic investigations are in the range of 0.1-100 Hz. The curves for 37 °C and 50 °C are almost constant in this range, which basically indicates similar rearrangement conditions for this specific parameter set of temperature and frequency. Considering this, accelerated tests for 50 °C could be performed with a frequency of 10 Hz, for example. A test at 75 °C would not provide reliable results, since the temperature is in the glass transition range. In addition, it is evident from the master curve that very high frequencies have to be achieved for a measurement in the same section of the curve, compared to the curve at 37 °C.

Overall, this method allows an estimation of desired parameters, but should not be applied with the purpose of providing exact temperature and frequency range due to averaging and curve shifting. However, since this method is used as a preliminary test, its application is still valid.

4 Conclusion

In the present study, 6 samples of a representative, biodegradable biomaterial were investigated by DMA. The viscoelastic properties determined by temperature and time dependence were shown. Furthermore, time-temperature-superposition principle was applied to the results of DMA to define test temperature and test frequency for dynamic mechanical fatigue tests. Similar to the results described in the literature for generating master curves, our study successfully described a semi-crystalline thermoplastic polymer reasonably well by the construction of master curves. The results indicate that a favourable selection of the test frequency directly depends on the selected test

temperature and correspondingly limits it due to the test bench capabilities.

Author Statement

Research funding: Partial financial support by the Federal Ministry of Education and Research (BMBF) within RESPONSE “Partnership for Innovation in Implant Technology” is gratefully acknowledged. Conflict of interest: Authors state no conflict of interest. Informed consent and ethical approval are not applicable.

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