Fourier-transform Dynamic mechanical thermal analysis - a new tool for the analysis of the thermo-rhelogical behavior of polymers and polymer sandwich composites

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Summary: A Fourier transform approach to dynamic mechanical thermal analysis is here outlined. The method uses raw instrument data acquisition, data oversampling and subsequent post-processing to evidence nonlinearities in the input/output signals. First results on polymers during time and polymer composite sandwiches during temperature sweep measurements are presented.

Introduction

Dynamic mechanical thermal analysis is a widely used method to characterize the viscoelastic response of polymers and polymer based composites. In most cases, the linear viscoelastic properties are thus investigated, however, the presence of nonlinearities in the materials' response, in certain test configurations measurements or while investigating nonlinear viscoelastic properties, are important for understanding the materials behavior [1]. Predominantly, failure in polymers and polymer based materials occurs due to fatigue, as ultimate stresses under cyclic oscillations are much lower compared to monotonic loading [2]. In addition, the local phenomena associated with periodic loading and failure in polymeric materials is of complex nature and can involve a superposition of creep, crazing, molecular orientation etc. In the case of polymer composites, temperature sweeps are a common method to asses the glass transition temperature with respect to the desired operating conditions. Moreover, the detection of defects during such tests, e.g. delamination, is of utmost importance for structural applications. In this framework, a novel, high sensitivity and versatile procedure for evidencing an analyzing nonlinearities during the testing of polymers and polymer based composite materials is here presented and preliminary results are summarized. The preliminary results consist of two commonly used characterization

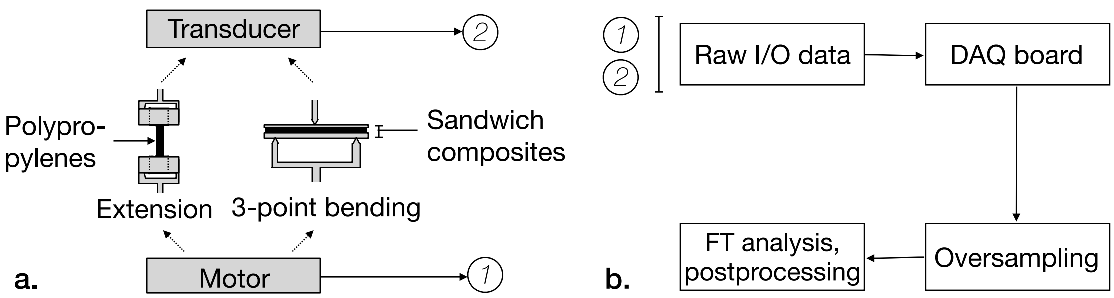

Figure 1: (a) Schematic of DMTA fixtures tested, i.e. extensional and 3-point bending, and materials tested, polypropylenes and sandwich composites. (b) Schematic of the Fourier-transform analysis approach that includes the instrument raw data acquisition, A/D conversion, the oversampling technique and subsequent post-processing.

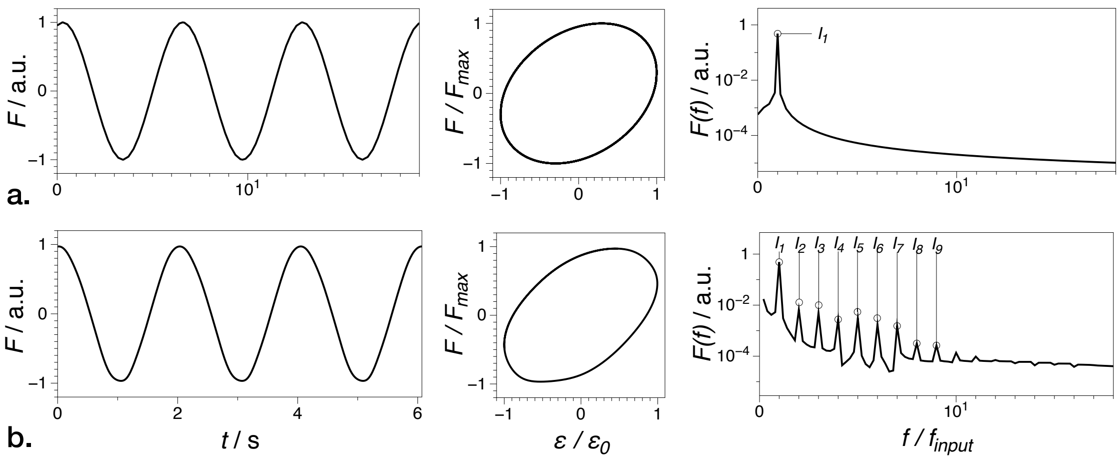

Figure 2: Examples of time series, Lissajous-Bowditch representations and associated Fourier spectra for (a) a sinusoidal material response and (b) nonlinear materials response. In the latter case, the time series consist of experimental data on sandwich composites enhanced (via smoothing and filtering) to emphasize the presence of the higher harmonics.

techniques, namely time sweep measurements in extension of polymeric materials and the temperature sweep in a 3-point bending fixture of sandwich composites for structural applications, Figure 1.a.

Materials and methods

The analysis method proposed is based, Figure 1.b, on the raw data acquisition of instrument input/output signals using a National Instruments data acquisition board and a LabVIEW routine. The oversampling technique is applied to improve the accuracy of the signal, i.e. signal to noise ratio, and provide insight into the mechanical nonlinearities exhibited [3]. The data is then post-processed using Fourier transformation and nonlinearities are evidenced via the higher harmonics present in the Fourier spectra, see Figure 2 for examples of a linear and nonlinear signals and associated Fourier spectra. The normalized intensities of the higher harmonics, their position and peak integrals can thus be monitored as function of time. More advanced data interpretation methods are readily applicable in the post-processing stage [4], however in this study only the dynamics of the detected higher harmonics is investigated using a transient (moving window) Fourier-transform approach. The experimental protocol was implemented on two different instruments, a Gabo Eplexor 150N (150N transducer; extensional fixture) and a Rheometrics RSA II (3-point bending), showing the versatility of the method.

Three polypropylene samples, i.e. homopolymers with and without ethylene comonomers (LyondellBasell), were subjected to time sweep testing using an extensional fixture. Time sweep measurements were performed in the linear (σ_{dyn} < 0.6 MPa) and weakly nonlinear viscoelastic regimes (0.6 < σ_{dyn} < 4.56 MPa), while keeping the other variables, i.e. frequency (20 Hz, 106 cycles), static load (σ_{stat} = 2.5, 5.5 and 6.5 MPa) and temperature (80°C), constant. In the results section the polypropylenes are labeled PP1, PP2 and PP3 corresponding to a pure homopolymer, and increasing amount of ethylene as comonomer, respectively.

A polymer - metal sandwich composite (Lamera A.B.) was investigated using temperature sweep tests, in relation to the glass transition temperature and associated sample integrity, i.e. occurrence of defects. The sandwich consists of two stainless steel facings of 0.15 mm in thickness with a total sandwich thickness of 1 mm. The sandwich core consists of layers of polymeric adhesive on the inner part of the facings holding in between polymeric fibers perpendicularly oriented to the laminate plane (see also Figure 4.a ahead). This results in a lightweight, formable composite with damping properties, suitable for a wide range structural applications. The temperature sweep test was performed starting from room temperature up to 100°C, with a temperature ramp rate of 1°C/min and an applied frequent of 0.5 Hz. The 3-point bending configuration used has a span of 48 mm and a width of approximately 10 mm.

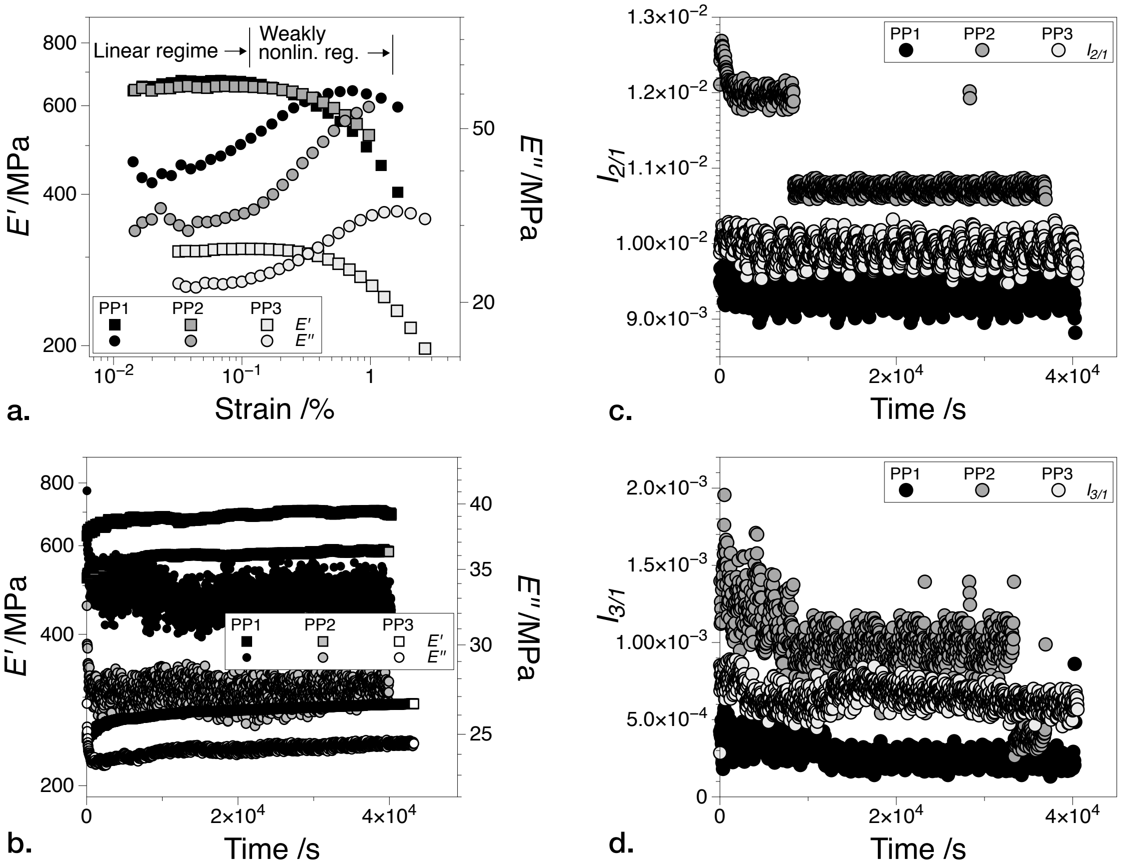

Figure 3: The time sweep analysis of the polypropylene samples tested: (a) example of strain sweep showing the linear and weakly nonlinear regions, (b) time sweep results showing the evolution of the dynamic moduli, (c) time sweep results showing the dynamics of second harmonic, $I_{2/1}$, and (d) of the third harmonic, $I_{3/1}$, relative to the first fundamental, see also Figure 2.

The data in this case was reduced prior to the moving window procedure for the FT analysis, and a number of maximum 5 cycles/dataset were analyzed due to avoid transient effects.

Results and discussion

The FT-DMTA analysis of polypropylene samples during time sweep tests is summarized in Figure 3. For testing, two strains were chosen corresponding to a linear and weakly nonlinear regime based on initial strain sweep measurements, Figure 3.a. Higher harmonics in extension were detected for both strains, with the linear results here shown. The dynamic moduli obtained are presented in Figure 3.b. Up to four higher harmonics, $I_{2/1}$, $I_{3/1}$ and $I_{4/1}$, in the frequency spectra could be accurately distinguished, with $I_{2/1}$ and $I_{3/1}$ being shown in Figure 3.c-b. Preliminary interpretations of $I_{2/1}$, correspond to the samples' creep behavior whereas using $I_{3/1}$ two decades of readings are obtained, compared to the dynamic moduli. In both cases, it should be noted that the magnitude of the higher harmonics does not correspond to the same ordering as for the magnitude dynamic moduli tests. While increasing complex modulus indicates the presence and the increase of ethylene comonomer content, with increasing higher harmonic magnitudes the samples follow the increase in polydispersity index, with PP1 and PP2 having identical molecular weight.

The FT-DMTA analysis of the composite sandwiches during temperature sweeps is summarized in Figure 4. For exemplification of a delamination process, a sample with a low adhesive glass transition temperature, $T_g \cong 50°C$, was chosen. At temperatures comparable to T_g and higher, a delamination process is observed at the interface between the adhesive and the metal facing, Figure 4.a. The temperature sweep was performed at strains within the linear regime, similar to the results in Figure 3. The resulting dynamic moduli are presented in Figure 3.b, showing the expected T_g. The development of nonlinearities in the output force

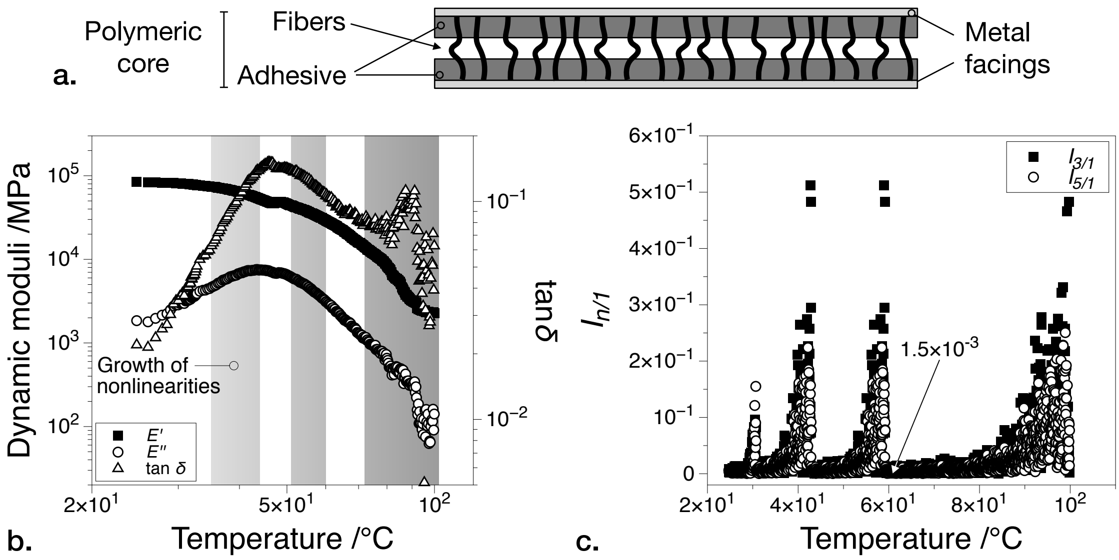

Figure 4: Temperature sweep analysis of composite sandwiches for structural applications: (a) composite structure and visual example of delamination at the adhesive - metal facing interface for temperatures $T \gtrsim T_g$, (b) dynamic moduli during temperature sweep and (c) the onset of nonlinearities via the third and the fifth higher harmonics, $I_{3/1}$ and $I_{2/1}$.

signal is marked on the diagram with the corresponding higher harmonics being detailed in Figure 4.c. Thus, nonlinearities are detected with increasing E'' en route to T_g as well as when the a maximal of rate of change in E'' is observed, with vanishing nonlinearities around T_g. The presence of nonlinearities could be generated by microstructural changes in the polymeric core as both constituents have approximately the same T_g. However, we note that their maxima is accompanied by an abrupt increase in the input (strain) nonlinearities, whereby both I/O signals revert to linear behavior. Nonlinearities detected towards the end of the test (three decades in $I_{3/1}$) were associated through visual observations to a delamination process at the facings-interface.

Conclusions

A versatile, high sensitivity procedure based on Fourier transformation for the detection and analysis of nonlinearities in dynamic mechanical thermal analysis tests was here outlined. Applications to polymeric materials and sandwich composites subjected to time and temperature sweep measurements were presented. The methods shows promising results with respect to enhancing the accuracy of the measurements, establish correlations based on the molecular properties of polymers as well as for the detection of nonlinearities associated to the occurrence of defects, i.e. delamination, in composites.

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References

[1] Golden, H.J.; Stragnac T.W., Schapery R.A. *Transactions of the ASME*, **1999**, *66*, p 872-878.
[2] Oswald, T.; Menges, G. *Materials science of polymers for engineers*, 3rd ed.; Hanser Publishers: Münich, Cincinnati, 2012; p 112
[3] van Dusschoten, D.; Wilhelm, M *Rheologica Acta* **2001**, 40, 395-399.
[4] Hyun, K.; Wilhelm, M.; Klein, C.O.; Cho, K.S.; Nam, J.G.; Ahn, K.H.; Lee, S.J.; Ewoldt, R.H.; McKinley, G.H. *Progress in Polymer Science* **2011**, *36*, 1697-1753.