Thermal properties of polymers via molecular dynamics simulations and thermal analysis

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Introduction

Molecular dynamics (MD) simulations and advanced multi-frequency temperature-modulated differential scanning calorimetry (TMDSC-TOPEM®)[1] provide a versatile, albeit difficult-to-master tool combination for materials design and characterization. Both methods have been previously successfully applied in polymer studies, however, emerging new bio-based polymers call for more research and mastery of these tools. Herein, we present our first results on thermal properties of poly(oxyethylene) (POE) and polyglycolic acid (PGA) using MD and/or TMDSC-TOPEM®. Our goal is to better understand the temperature-dependent and time-dependent processes in polymer behaviour and separate the overlapping events in the glass transition region. Moreover, we aim at a more comprehensive and careful data analysis with parallel MD simulations and DSC experiments.

Models and Methods

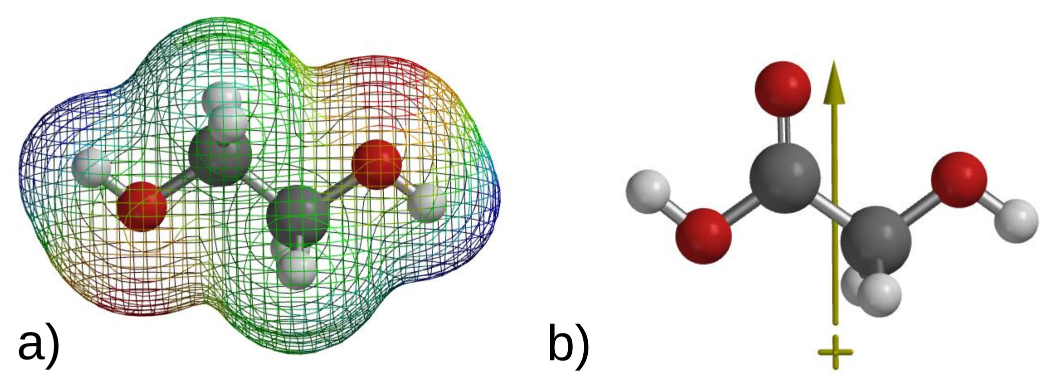

Figure 1. *Monomer structures for the constitutional repeating units (CRU) of a) POE and b) PGA. The direction of the non-zero electric dipole moment shown for POE.*

To retrieve the glass transition temperature (T_g) for the amorphous morphology of POE, GROMACS software version 2020.5,[2] with the OPLS-AA force field, was used for the MD simulations. In 6×6×6 nm^3 cubic simulation boxes, either 144 chains with 12 CRUs or 25 chains with 50 CRUs were cooled within 500–50 K using both stepwise and continuous cooling (annealing)[3].

Dynamic DSC and TOPEM measurements on semicrystalline, commercial polymers were done using Mettler–Toledo DSC1 thermoanalyzer with liquid nitrogen cooling, N_2 as the inert and purge gases, and 40 μl Al crucibles. POE samples were cooled (278–176 K) and PGA samples heated (273–385 K) with the rate of 1 K/min using 1 K pulse height in the TOPEM runs.

Results

MD simulations of POE

Fig. 2 illustrates the simulated system stabilized at 200 K after a stepwise temperature descent from 500 K. The average densities for the stepwise and continuous processes from 500 K to 50 K are presented in Fig. 3 and 4, respectively. Three thermal sections can be distinguished. In the stepwise cooling glass transition region begins at ca. 285 K and ends at ca. 210 K, which is recorded as T_g. Similarly for the continuous annealing, the transition occurs at 206–284 K, yielding T_g of 207 K.

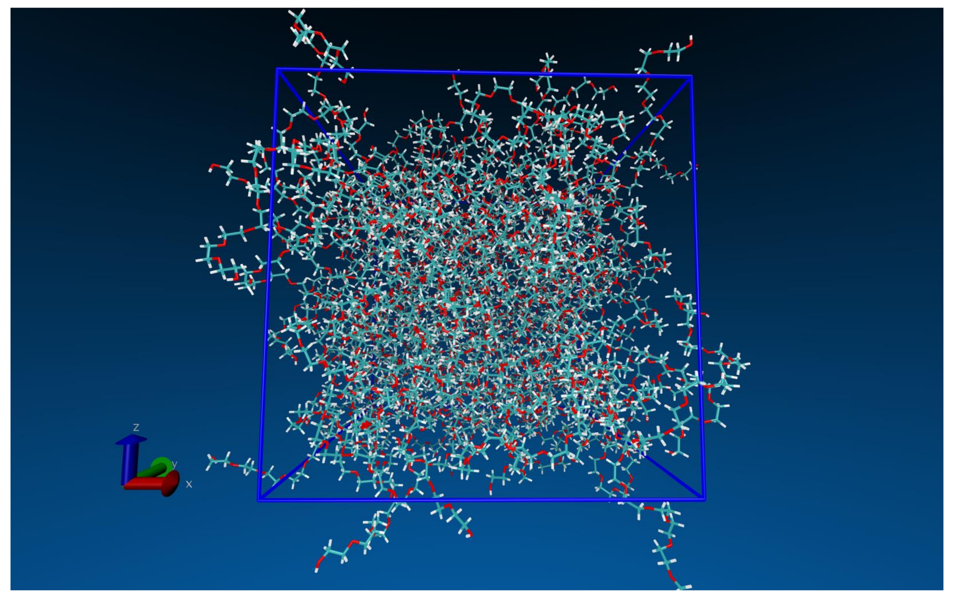

Figure 2. *A snapshot of the system consisting of 25 POE chains in a periodic MD simulation box after 5 ns at 200 K.*

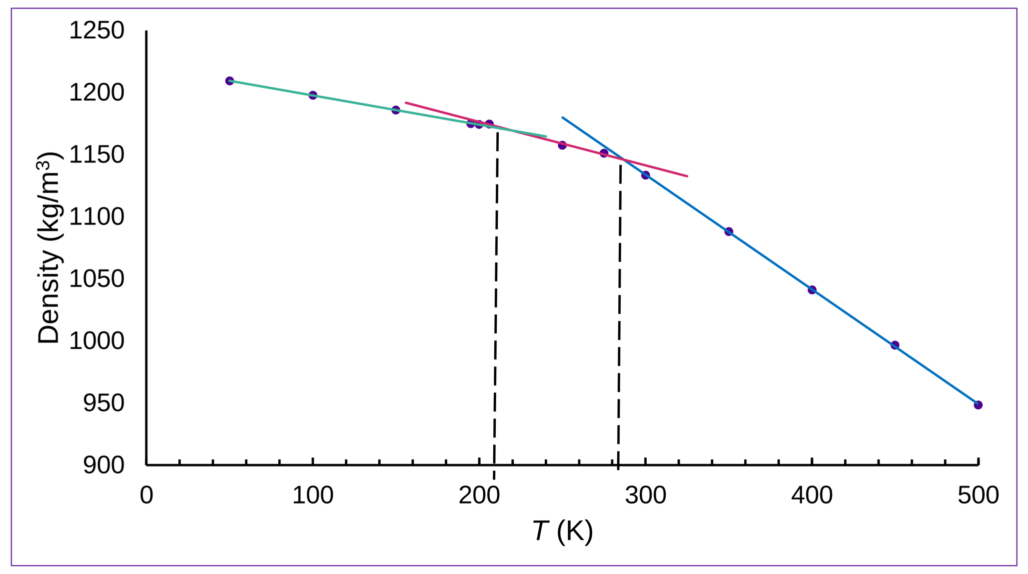

Figure 3. *Average densities of POE at different temperatures via simulated stepwise cooling.*

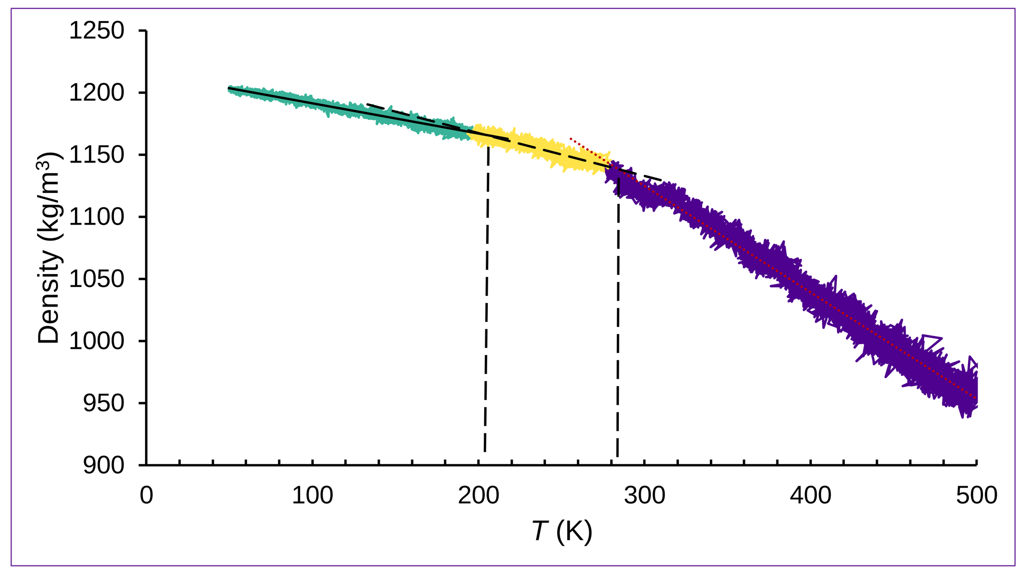

Figure 4. *Average densities of POE at different temperatures via simulated continuous annealing.*

TOPEM analyses

The total, reversing and non-reversing heat flow curves, and the quasi-static heat capacity curve (cp0) were calculated for POE and PGA from the original TOPEM curve, presented for POE in Fig. 5 and 6a. The complex, cp*, and in-phase (cp', not shown) heat capacity (Fig. 6a) and phase (Fig. 6b) curves were determined from the cp0 curve. The glass transition evaluated from the cp0 curve is free from overlapping thermal effects. The cp' curve shifts to a higher temperature with increasing frequency (Fig. 6), as expected. The phase curve reflects changes in heat transfer within the sample.

Conventional DSC yields T_g of 312 K with an enthalpy relaxation peak at 315 K for PGA. This is in good agreement with the values determined via TOPEM from the reversing heat flow (311 K) and cp0 (310 K) curves, without overlapping thermal effects. Total heat flow and non-reversing heat flow curves show a wide endothermic peak at 318 K (-2.7 J/g), which resembles melting, visible also in the 1st DSC scan, overlapping with T_g. The main results are summarized in Table 1.

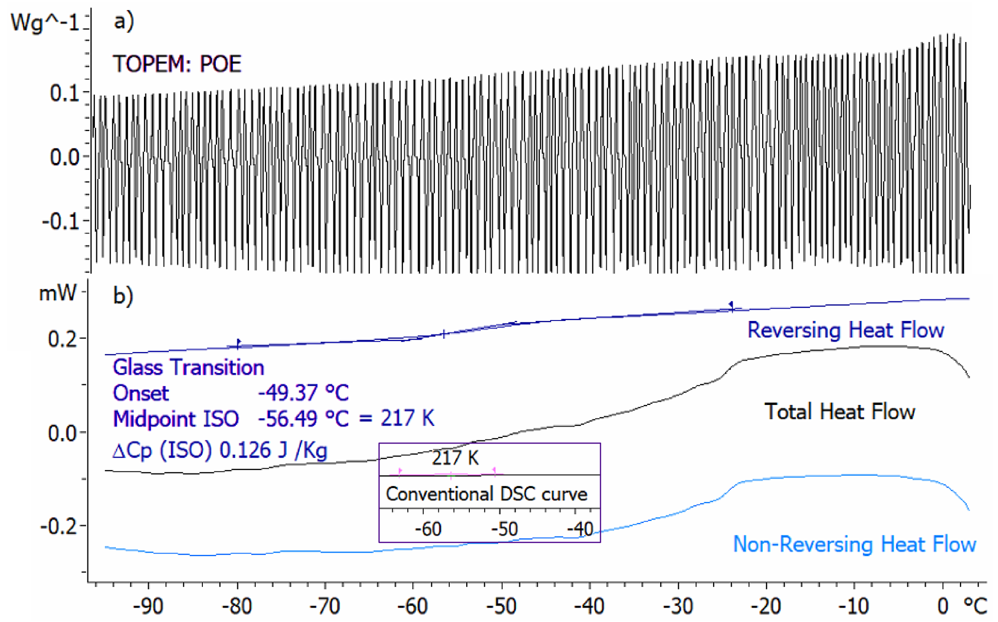

Figure 5. *a) TOPEM and b) heat flow curves with the conventional DSC curve in the insert.*

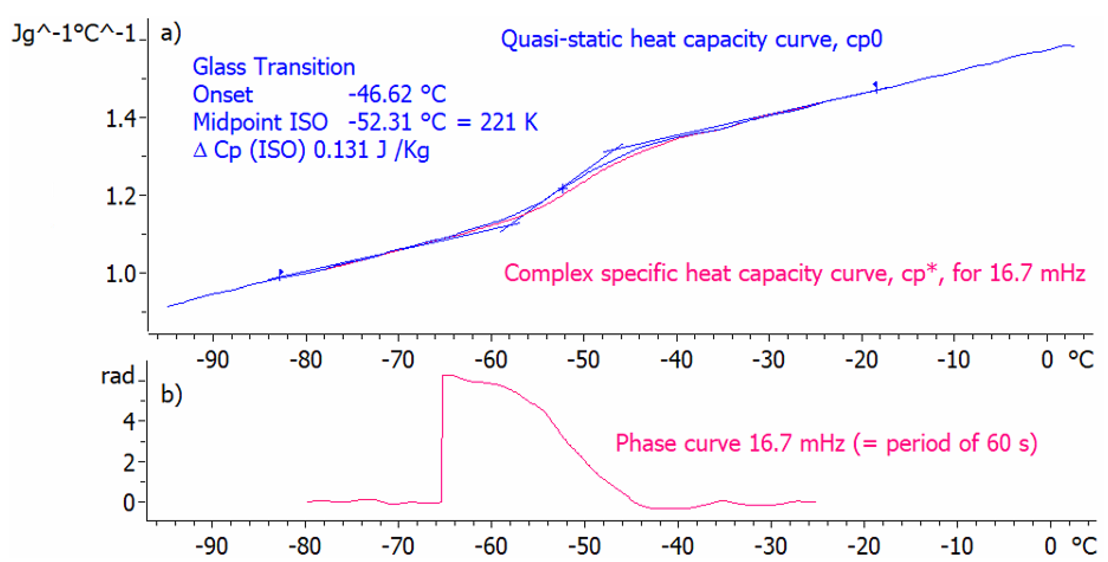

Figure 6. *a) Heat capacity and b) phase curves calculated from the TOPEM curve.*

Table 1. *T_g (K) values simulated for POE with MD, measured for POE and PGA with TOPEM (reversing heat flow), and reported in literature (ref.).*

Polymer	MD (step)	MD (cont.)	TOPEM	ref.
POE	210	207	217[a]	190– 210[4]
PGA	*	*	310	309– 318[5]

* Force field under development. [a] Sigma-Aldrich: 206 K.

Conclusions

The T_g values predicted by the MD simulations for POE complement our conventional DSC and TOPEM measurements. The quasi-static heat capacity curves show frequency dependence in the glass transition region confirming the interpretation is correct. The simulated T_g-curves contain three distinguished thermal transition regions, with three slopes. Errors may occur in the interpretation of data, if only two slopes are used, leading to too high T_g values. Both the stepwise and continuous cooling simulations yield similar results. PGA shows overlapping events in the conventional DSC curve, which can be separated by TOPEM yielding T_g within the range reported in literature.

Acknowledgements

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