**Thermodynamic prediction of the glass transition temperature in polymers and polymer blends**

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**Highlights**

* Calculation of the glass transition temperature with an equation of state.
* Comparison of the results with experimental data from the literature.
* Application of the theory to various examples e.g. miscible/immiscible blends.

**1. Introduction**

The development of reliable approaches for the prediction of the thermodynamic properties of polymer systems is crucial for the reasonable design of polymer materials and polymer processing in a wide range of polymer applications (for example composites, electronics, food, controlled drug delivery systems, medical devices). Glasses are disordered materials that lack the periodicity of crystals but behave mechanically like solids.

The assumption that the glass transition is basically thermodynamic in nature was used to derive a theoretical framework for the calculation of the glass transition temperature (TG) of polymers, copolymers and polymer blends [1,2,3]. The theory is a synthesis of a thermodynamic equation of state suitable for polymers, the generalized entropy theory for glass-formation in polymer materials, and the rigorous Kirkwood-Buff theory for concentration fluctuations in binary mixtures [2,3].

**2. Methods**

In the present contribution the above described framework is applied in order to compare the theoretical results with experimental data taken from the literature. Hereby the Sanchez-Lacombe equation of state (SL-EOS) [4] was used, because the pure-component parameters for several different polymers (polystyrene, (PS); poly(vinyl methyl ether), (PVME); poly(methyl methacrylate), (PMMA); poly(p-phenylene oxide), (PPO)) as well as for the statistical copolymer consisting of styrene and acrylonitrile (PSAN) are available. Unfortunately, the parameters for polyacrylonitrile (PAN) are not available, because no PVT (pressure, volume, temperature) data can be measured with high accuracy. The reason for this finding is the thermal instability of this polymer. Therefore, the pure-component parameter for PAN were estimated using PS and PSAN data simultaneously.

**3. Results and discussion**

Using the above mentioned theoretical framework [1,2,3] the TG of pure polymers was calculated as function of the molecular weight, and compared to experimental data. The analysis shows, that one adjustable parameter per pure polymer is required to match experimental TG data. Regarding the molecular weight dependency, the theory predicts correctly that the TG tends towards a limiting value for high molecular weight polymers. This concept can also be applied to statistical copolymers (i.e. PSAN), where the TG is predicted as function of the chemical composition in good agreement with experimental data taken from the literature [5].

Furthermore the theoretical method can be applied for polymer blends, where the Kirkwood-Buff formalism serves for the determination of the concentration fluctuation. These calculations were performed for immiscible blends made of PS and PVME, where the TG was investigated as function of blend composition. The results are compared with experimental data [6,7] in Figure 1. Blends made of PS and PPO serve as an additional example for miscible blends, where experimental data are taken from [8].



**Figure 1.** Calculated (solid line) and experimental data from the literature (squares [6], triangles [7]) for the glass transition temperature in a PS-PVME blend.

**4. Conclusions**

It is shown that the calculation of TG in polymers and polymer blends can be done with an equation of state e.g. SL-EOS. Hereby the application of the Kirkwood-Buff formalism allows to combine thermal and concentration fluctuations in polymer blends. The results are in good accordance with experimental data and can be applied for different systems e.g. miscible/immiscible polymer blends.

**References [Calibri 10]**

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