HIGH-PRESSURE CALORIMETRY: THERMOPHYSICAL PROPERTIES OF GASES AND POLYMERS

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During the last decades polymers were important materials for technological progress of our western consumption society. The importance of advanced polymer materials is still increasing and polymers are not only used for packages anymore, but for high-value products such as high-voltage cable insulations, solar cell coatings or medical applications. Due to that, the necessity for optimized and energy efficient processes including a proper waste treatment is increasing. In 2015 worldwide plastic productions were at 322 million tons, mostly common polymers are Polypropylene (PP) and polyethylene (PE) with a content of 48.5%. [1] Some of the production processes, for example low-density polyethylene (LDPE), are performed at high pressures and temperatures of up to 3000 bar and 300 °C. To optimize respective processes, simulation-models have been used more commonly during the last years. Computational models are a comparatively cheap and safe alternative in comparison to actual changes in the process and can be used to test new concepts or recipes. Beside kinetics, simulation-models are based on thermophysical properties such as density or heat capacity. Correlations of these parameters are applied to describe the heat balance of the process and therefore influence the conversion during a simulation-run. To describe a process as detailed as possible, correlations of applied components like monomers or polymers have to rely on exact substance data. Although the temperature dependence of different properties is described well by currently applied correlations, a pressure dependence is mainly achieved by extrapolating fragmentary datasets. These data-sets were partly determined at atmospheric pressure and have not been evaluated further since their publication during the second half of the last century, which makes an application at the demanding polymerization process conditions rather imprecise. Consequently, for an improvement of such simulation-models new and exact substance data at the respective process conditions are required.

In this work high-pressure calorimetry has been used for this purpose. Regular calorimetric devices, such as the DSC, have been applied to determine thermophysical properties at atmospheric pressure, but they are not suited for measurements at higher pressures. Such conditions require precise sensor technologies combined with rather massive mountings to withstand the extreme conditions. One device, which merges these properties is the transitiometer. This special Tian-Calvet calorimeter can withstand pressures up to 4000 bar without a decrease in precision. In a measurement one parameter (temperature, pressure or volume) is kept constant, the second one is varied with time and the third is measured as a function of the first two.

Applying a pressure program in the transitiometer, expansion coefficients of different gases and polymers could be calculated when evaluating the measured difference heat fluxes. Coming from a temperature and pressure dependence of expansion coefficients, heat capacities could be determined in both dependencies as well. While testing different experimental setups, a pressure- and temperature dependence of densities of polymers could be calculated as well. In heat capacities of carbon dioxide, ethane or ethene a maximum in the temperature dependence in all measured pressures could be observed, which cannot be seen in methane or nitrogen. Beside a temperature-dependent maximum, a pressure dependent maximum is indicated in those molecules as well. Those maxima might be first experimental evidence of results regarding different molecular-dynamic simulations. Here, phenomena in the super-critical area of a phase diagram so called “Widom-Line” and/or “Frenkel-Line” that indicate a “pseudo” phase transition are predicted. That phenomena divide assumed homogeneous phase of the supercritical area, in a gas-like and a liquid-like region. [2]

Next steps will be to validate measured data sets and to compare different types of polymers, including homo- and co-polymers. Additionally, it will be necessary to investigate not only pure substances such as polymers or gases, but to examine excess- and solubility effects between different molecules. First indications of such effects have already been observed since melting points of polymers change with pressure and different pressure media. Such effects might also influence already determined heat capacities or expansion coefficients. Another important task in the future will be the investigation of peroxide kinetics in dependence of pressure, temperature and solvent viscosity.

[1] PlasticsEurope, 2016, http://www.plasticseurope.org/documents/document/20161014113313-plastics_the_facts_2016_final_version.pdf
[2] T. Bryk and T. Scopigno*, J. Phys. Chem. Lett.*, 2017, 8 (20), pp 4995–5001.