

Editorial corner – a personal view

The ‘reptation model’ and the melts of condensation polymers

S. Fakirov*

The University of Auckland, Department of Mechanical Engineering, Centre for Advanced Composite Materials, Auckland, New Zealand

Diffusion is a universal phenomenon taking place in gases, liquids and even in solids. The diffusion process in low molecular weight substances involves whole molecules, that is, the complete molecules move not only parts of them. The mass transfer could be represented as a process consisting of ‘jump-like’ steps. Dealing with polymers the described diffusion mechanism is not applicable because the energy needed for ‘jumping’ of the whole macromolecule is much larger than the energy needed for breaking the chemical bonds resulting in a chemical degradation of macromolecules.

This problem was solved by de Genne (<https://doi.org/10.1063/1.1675789>) and Edwards (ISBN: 9780198520337) suggesting the fundamental concept of ‘reptation model’: the polymer chain is assumed to be confined in a hypothetical tube, the contours of which are defined by the position of the entanglement points in the network and the single polymer chain may move in a snake-like fashion among them (<https://doi.org/10.1063/1.1675789>).

Condensation polymers, contrast to the polyolefins, are distinguished by their inherent property to react with each other via additional (post) polycondensation and/or the exchange- (trans) reactions. Studying the new phenomenon of chemical healing (<https://doi.org/10.1002/pol.1984.180221208>) as a result of chemical interactions at elevated temperatures in condensation polymers, the concept of ‘chemically released diffusion’ was formulated (Polymer Commun. 26 (1985)137–139), that is, the mass transfer in condensation polymers at elevated temperatures taking

place parallel to chemical reactions mostly of exchange type.

Measurements of the interchain transreactions rate between deuterated and non-deuterated PET chains at 280 °C resulted in approximately 10 transesterification reactions occurring per molecule per minute (<https://doi.org/10.1021/ma00171a041>). At 450 °C the rates are more than 100 ester interchange reactions per chain per second (<https://doi.org/10.1021/ma00208a041>)! It follows that the reacting units between the moments of bond breakage and re-establishment the units can move, diffuse. However, they move as single (or small blocks of) repeating units and not as whole macromolecules because the macromolecules as long real chains do not exist anymore. In this situation, it is hardly reasonable to use the ‘reptation model’ for explaining the diffusion mechanism in melts of condensation polymers. It seems more realistic to accept the diffusion mechanism characteristic for the low molecular weight substances since the independent kinetic units in melts of condensation polymers are not the macromolecules but the individual repeating unit or their small blocks (<https://doi.org/10.1016/j.progpolymsci.2018.09.003>).



Prof. Dr. Stoyko Fakirov
Member of the Executive Editorial Board

*Corresponding author, e-mail: s.fakirov@auckland.ac.nz
© BME-PT