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POLYMER CRYSTALLIZATION AND AVRAMI EQUATION

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ABSTRACT
This work is focused on the simulation of polymer crystallization based upon the Avrami equation. The Avrami equation is routinely used as a tool for the crystallization kinetics description. The equation can be written in the form: 1 - X_c = exp (-Kt^n) where X_c is the crystalline volume fraction developed at time t and constant temperature, and K and n are suitable parameters depending on crystallization conditions. In this work, several spherulitic structures were simulated using various time-dependent nucleation intensity and growth rate. The significance of the parameters for the structure variation was described and discussed.

1. INTRODUCTION

Properties of polymers are heavy influenced by they structure which is determined by process of crystallization. An useful tool to understand and predict the polymer structure is the numerical simulation. The theory of crystallization kinetics is based on the appearance and growth of geometrical objects which growth over the volume during the transformation. Theory of this process is given by Avrami [1] and improved by Evans [2].

1.1 The Johnson-Mehl-Avrami model

The standard Johnson-Mehl-Avrami model describes the isothermal transformation from a mother phase α to a daughter phase β, by nucleation (the process by which the formation of a new phase begins), growth, and impingement (the restriction of transformed region growth by other transformed regions). This theory is based on three main assumptions: an infinite volume *V* available for transformation, random nuclei positions (nuclei positions are Poisson point process), and isotropic growth of transformed regions. Specific simplifying assumptions have also been made about geometry and kinetics of nucleation and growth, in order to derive analytical solutions for special cases, such as zero-nucleation rate (pre-existing nuclei), constant nucleation rate, linear growth velocity, diffusion-limited growth, and growth of crystals in needle- or plate-like configurations [3].
There are two special cases:
1) the nuclei are predetermined; that is, they all develop at once on cooling the polymer to the temperature of crystallization (fig. 1),
2) there is sporadic nucleation of the spheres (continuous nucleation with a constant rate), nuclei born inside older cells are rejected (fig.2).
In the first case the growth process lead to Voronoi tessellation. Cells are convex, bounded by convex polygons. In special case if generators positions are random independent (Poisson point prosess), tessellation is called Poisson-Voronoi tessellation. In the second case the growth process lead to Johnson-Mehl tessellation, cells can be non-convex.
The Avrami equation provides useful data on the overall kinetics of crystallization:

$$1 - X = \exp\left(-Kt^n\right), \tag{1}$$

where t is time, X is the volume fraction of daughter phase β and 1- X the volume fraction of mother α–phase. Parameters K and n depends on phase transformation mechanism. The equation has been derived for spheres, discs and line segments, representing three-, two- and one-dimensional form of isotropic constant rate growth.
The values of exponent n can be expressed by formula $n = m + g$, where m is dimension of growth (m = 3 for spatial, m = 2 for planar and m = 1 for linear growth) and g = 0 for instantaneous nucleation and g = 1 for random (sporadic) nucleation.

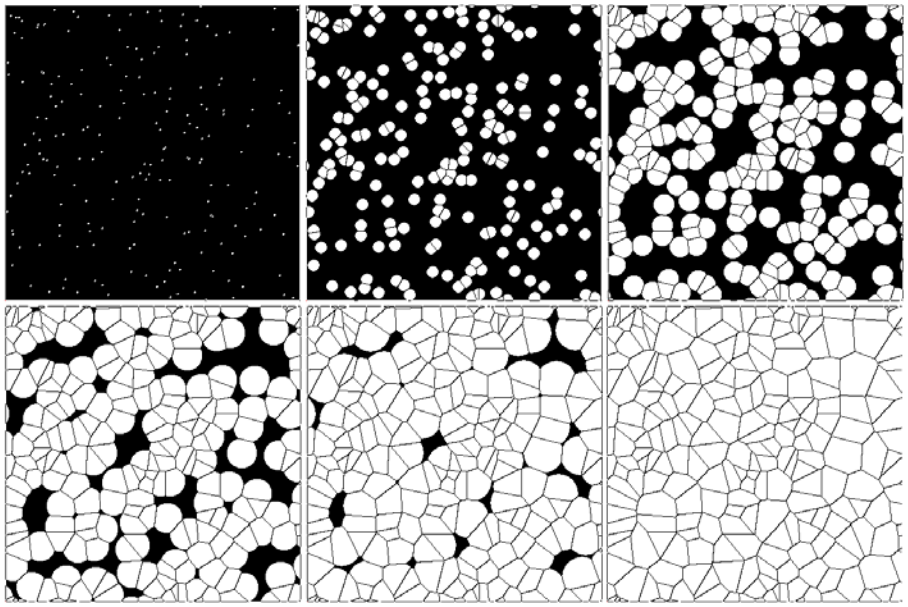

Figure 1: Growth model of planar Poisson-Voronoi tessellation – all nuclei develop at start of process

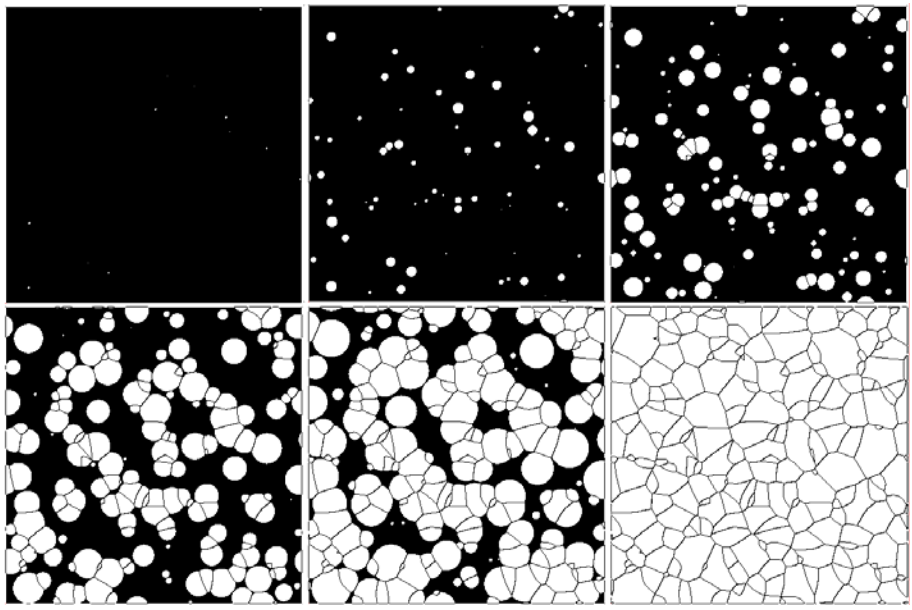

Figure 2: Growth model of planar Johnson-Mehl tessellation – nuclei develop randomly continually

2. SIMULATION

The phase transformation is numerically simulated on computer. A set of planar or spatial nuclei is generated. To each nucleus a coordinates and birth time are assigned. The two- or tree-dimensional space region is approximated by matrix of 1000^2 or 1000^3 points. In this region a set of about 200 nuclei in 2D and 2000 nuclei in 3D case was located. For each space point a time required for nucleus growth to this point is computed and the index of generator with minimal time and this growth time

are assigned to this point. The growth velocity is isotropic and can be linear function of time to describe possible temperature change during process. To avoid a boundary effects the periodic boundary conditions are applied (fig. 3).

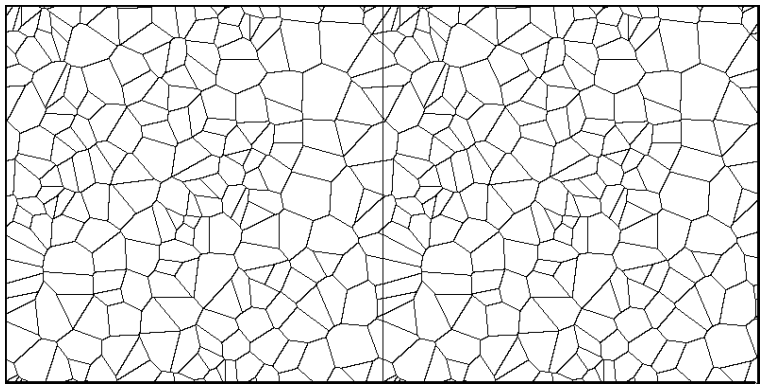

Figure 3: Periodic boundary conditions – two the same square planar simulated tessellations annexed together, note that cells on one boundary continues at the opposite one.

3. RESULTS

Two kinds of tessellations based on both type of nucleation processes mentioned above were simulated. The time-dependence of mother phase ratio was observed. Figure 4 shows the planar case, figure 5 the spatial case; versions a) describes instantaneous nucleation, versions b) the sporadic nucleation. Note, the declination of mother phase at start of transformation: for a) version begin immediately – all nuclei start to growth, for b) version the declination is belated – nuclei must foremost born ant then start the growth. The graph points are values obtained by computer simulation, lines are fitted to simulated data using formula (1).

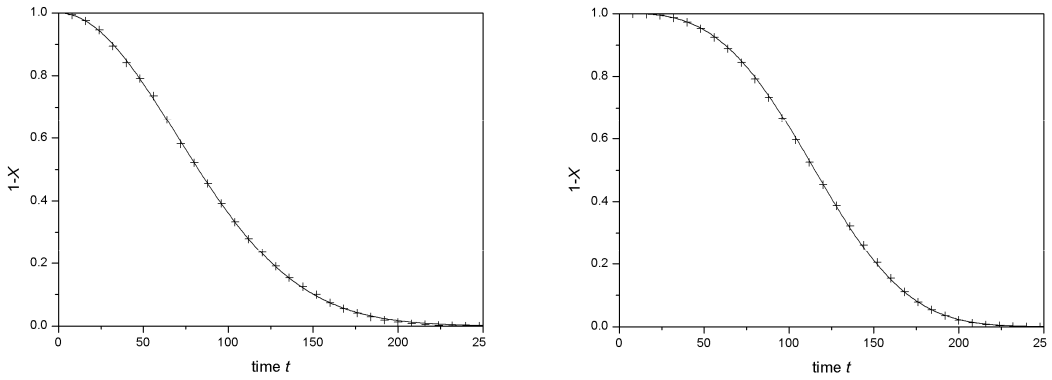

Figure 4: Time dependence of area ratio of mother phase.

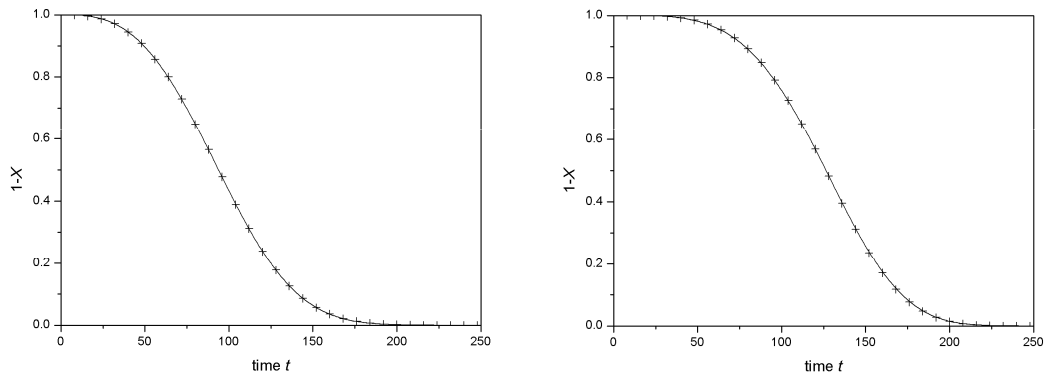

Figure 5: Time dependence of volume ratio of mother phase.

The following table collect the parameters of curves fitted to simulated data

model	**Avrami's *n***	**fitted *n***
planar, instantaneous nucleation	2	2.00
planar, sporadic nucleation	3	3.07
spatial, instantaneous nucleation	3	2.94
spatial, sporadic nucleation	4	3.93

4. CONCLUSION

We have chosen to start from basic principles of Avrami's approach. First, it ensures the consistency of the whole formulation. Then it gives a more precise description of the nucleation event. From this base we can build more general events as is time-dependence of nucleation or growth rate. The influence of these parameters on final spatial tessellation will be studied in the next step. The spatial properties of tessellation are usually inaccessible by direct measurement. We would like to simulate planar sections of spatial tessellations and connect their properties with nucleation conditions.

5. ACKNOWLEDGEMENTS

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6. REFERENCES:

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[3] Haudin, J.-M., Chenot, J.-L.: Intern. Polymer Processing XIX 3, 2004, p. 267