

INVESTIGATION OF THE NUCLEATION PROCESS IN A BI-COMPONENT SYSTEM USING MONTE CARLO SIMULATION

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Abstract. Using Monte Carlo simulations, we investigated the instantaneous nucleation of polymeric blends and we found that the kinetic is well described by the Avrami equation. We calculated the overall crystallization rate constants and the Avrami indices and we made a statistics of the radii of the generated spherulites.

Key words: instantaneous nucleation, Avrami equation, crystalline polymers, Monte Carlo simulation.

1. INTRODUCTION

Physical, chemical and technological properties of solid polymers are strongly influenced by their structure, determined by their degree of crystallinity and also the kinetic of crystallization [1–6]. It follows that explanation of the crystallization mechanism of this class of materials is a very important goal for theoretical, experimental and applicative domains.

The main macroscopic parameter describing the crystallization of polymers is the crystalline fraction of the material, defined as the ratio between the volume of the crystallized region and the total volume of the material [1–8]. This parameter depends on time and it is based on the apparition and expansion of the crystalline regions in the volume of the polymer. It is also known the fact that the polymer molecules consist in a very large number of monomers, a crystalline polymeric domain being created by folding the polymeric chain [2, 5, 7, 8]. On the other hand, in such a domain, may also enter chain portion from other macromolecules, the entanglement giving rise to a very complicated landscape of energy barriers. Therefore, there is a number of monomers that cannot enter in the crystalline state. The remaining monomers belonging to different macromolecules remains in the amorphous state, in fact, a crystalline polymer being only semicrystalline [5].

Experimentally, the study of the polymer crystallinity is realized by X-ray diffraction, NMR and Raman scattering, electron microscopy, polarized light microscopy, density and calorimetric methods [5, 7].

The theoretical model that is widely used to describe the polymer crystallization is based on the *Kolmogorov-Johnson-Mehl-Avrami*, KJMA, theory [9–13]. The method of Avrami macroscopically describes the mechanism of the polymer crystallization and rely on some simple assumption regarding the apparition and growth of the crystalline domains. The hypotheses of the Avrami model were described elsewhere, [5–8, 14–16], the most important being the apparition and growth of the crystalline domains which expand in the volume of the polymer. In the model, the crystalline domain first appears as a geometrical point in space called nucleus, the nuclei being randomly and homogenous disposed in the volume. These points symmetrically grow with the same velocity. In the original theory of Avrami, two growing nuclei may mutually invade each other.

There are two methods to address the crystallization of polymers [5, 6, 8]:

- instantaneous nucleation, also called athermal nucleation, when all the nuclei appear at the beginning of the crystallization, are uniform distributed in the volume of the probe and start to spherically grow at constant velocity;
- sporadic nucleation, also called thermal nucleation, where the nuclei are uniformly disposed in the volume of the probe and appear at a constant time rate and grow at constant velocity.

Despite the fact that the empirical method of the Avrami does not take into account the microscopic mechanism of the polymer crystallization, the results of the model are in very good agreement with the experimental facts [1–4, 7].

On the other hand, in the last decades, Monte Carlo and molecular dynamics simulations have become widely used tools in condensed state physics [17–20]. Because of the technical advance in the information technology, both hardware and software, computer simulation is used at a large scale in the investigation of the liquid crystals [20–22] and polymers [18–20, 23, 24], the results being in accordance with theory and experiment [25–29] as it is explained in [17].

In a series of paper, it was investigated nucleation of polymers using computer simulations [5, 6, 14–16], the results being in accordance with the prediction of the Avrami theory. In these papers, it was investigated both sporadic [5] and instantaneous regular polymer nucleations [6], nucleation processes in frustrated polymeric systems [14], instantaneous and sporadic nucleations in n -dimensional space [15, 16].

The previous obtained results offered us a very interesting image about the possibility to adapt the Avrami model to many practical situations, the main conclusion being that the Avrami equation has a universal behaviour and may also be used to explain results for very special crystallization systems.

One may ask the question if the Avrami model is still valid if we have a blend of polymers which compete to crystallize in the same volume. The situation is thoroughly discussed in [30, 31] for various type of polymeric blends. The interest in discuss such behaviour is because, beside copolymers, polymeric blends are of great interest in producing composites with special properties, used for polymer-based light emitting diodes, nanotechnology and other various applications [31–35]. On the other hand, computer simulations and numerical solutions of some mathematical complex situations is of great interest in soft matter physics [5, 6, 14–24, 36–40].

In the present paper, using Monte Carlo simulations, we investigated the instantaneous crystallization of a blend comprising two crystallizable polymers. In such case, it is expected a very complex behavior, due to the influence of both phases, each of them with its own properties [30]. Because of the multitude of possible effects of phase behaviour of the components, we restricted our investigation to so-called “coincident crystallization”, in which the two phases crystallize at the same time.

In the remaining of the paper, we will describe our model of the crystallization and the computer simulation method, followed by presenting the result of the simulations and discussions.

2. MODEL AND SIMULATION METHOD

As it is described in [5–8, 14–16], the classical method to analyze the kinetic of crystallization of the polymers is to record the time dependence of the crystalline fraction of the polymer, X_c and applying the KJMA theory, in order to find the crystallization parameters.

We consider here a coincident crystallization of a crystalline/crystalline blend of two kind of polymers, denoted by indices “1” and “2”, as it is described in [30], where experimental evidence of this kind of behaviour is reported.

In order to simulate the crystallization of this polymeric blend, we kept as much as possible the assumptions of the original Avrami method [5–8, 14–16], but adapted for a two component system:

- the volume of crystallization is homogeneous, implying that both kind of nuclei may freely appear; because we simulate the instantaneous nucleation, all the nuclei appear at the beginning of the run.

- all the nuclei of the same type spherically grows with the same velocity, giving birth to the so called spherulites [5–8, 14–16].

- two growing nuclei of the same type may mutually invade each other. In other word, the impingement phenomenon, as it is described in [8], is taken into

account only for different species, being an indication of the heterogeneous nucleation of the polymeric blend [30].

In the absence of the impingement phenomena, at any time instance, all the spherulites would have the same radius. This kind of behaviour was considered in our previous work [5, 6, 14–16], the simulation results being in excellent agreement with the Avrami equation [1–16] which theoretically describes very well the kinetic of crystallization, *i.e.* the time dependence of the crystallized volume fraction:

$$1 - X_c = \exp(-kt^n). \quad (1)$$

The above relation is valid for crystallization of a homogeneous (single) polymer.

n is the Avrami index, that, for instantaneous nucleation, is equal with the dimensionality of the space, in our case 3, because we considered the 3-dimensional crystallization [6–8]. For a sporadic nucleation, the Avrami index is equal with the space dimensionality plus one [5, 7, 8]. It follows that we should expect a value of 4 if we would consider the sporadic nucleation.

k is the overall crystallization rate and it is a quantity that, for instantaneous nucleation, depends on the growth rate v and on the number of nuclei per unit volume g [6–8]:

$$k = \frac{4}{3} \pi v^3 g. \quad (2)$$

In order to describe the crystallization process, it is necessary to obtain the overall crystallization rate constant, k , and the Avrami index, n . Usually, the Avrami equation is linearized by taking the double logarithm in equation (2) [5–8, 14–16]:

$$\ln[-\ln(1 - X_c)] = \ln k + n \ln t. \quad (3)$$

The advantage of the equation (3) is that it is linear in $\ln t$, with the slope equal with the Avrami index and its intercept is the logarithm of the crystallization rate constant.

Equation (1) implies that, for a sufficient long crystallization time, the fraction of polymer asymptotically tends toward 1. But, as we explained in the introductory part, even pure polymers are only semi-crystalline, the fraction of crystallized phase being less than unity [5, 8]. Sometime, in this situation, the Avrami equation is modified to

$$1 - \frac{X_c}{X_{c\infty}} = \exp(-kt^n), \quad (4)$$

where $X_{c\infty}$ is the final volume fraction of the crystalline polymer, quantity that can be experimentally determined [8].

For our two component system, because we denied the impingement between crystalline domains resulting from different polymeric kind, we cannot be sure that the above equations still stands. The main reason for that is the fact that two close spherulites of different kind hinder on to another to increase in time.

In the absence of a mathematical model for this situation, Monte Carlo simulation remains the solution of choice. Our simulation model consists of a cubic box of side L , where, at the beginning of the crystallization process, N_1 and N_2 nuclei randomly appear and begin to grow with velocities v_1 and v_2 . At all the following moments of time, the nuclei spherically grow with the velocity of its species, until the crystallization front encounter another one belonging to the other type.

At every time step during the simulation, we recorded the volume fraction of each crystalline fraction of polymers, X_1 and X_2 . These quantities were calculated as the ratio between the volume occupied by a certain kind of spherulites (taking account of allowed overlapping between spherulites of same type) and the total volume of the box.

As we explained above, because of the interdiction of intersecting between spherulites of different types, not all of them will have the same radius as in regular instantaneous nucleation [6, 8, 15].

It follows that the radius of all spherulites will have a distribution of sizes, which is worth to be determined, so, for each run, we also recorded the radius of all crystalline domains.

Because the procedure is very sensitive to randomness, the fluctuation of recorded quantities may be quite big, so it was necessary to take averages on at least 10 runs for each point, resulting relatively long calculations.

3. RESULTS AN DISCUSSIONS

Our model depends on four parameters: number of nuclei of each type, N_1 and N_2 , proportional with the number of nuclei per unit volume, g_1 and g_2 , plus the growth rates, v_1 and v_2 . Several combination of these parameter may exist and we investigated the influence of these parameter on the crystallized polymer fractions and on the distribution of radius of the spherulites.

3.1. INFLUENCE OF THE GROWTH VELOCITIES ON THE VOLUME FRACTIONS

First of all, we investigated the influence of the growth velocity on the crystallization kinetic of a symmetric polymeric blend with the same number of nuclei per unit volume. We made a first set of simulations for a cubic box

with $L = 10$, $N_1 = N_2 = 100$, $\nu_1 = 0.06$ and $\nu_2 = 0.01$. The length of the box and growth velocities are given in arbitrary units. For the same reason, the numbers of nuclei per unit volume are $g_1 = g_2 = 0.1$. During the runs, we recorded the volume fractions of crystallized regions, X_1 and X_2 , their time dependence being depicted in Fig. 1.

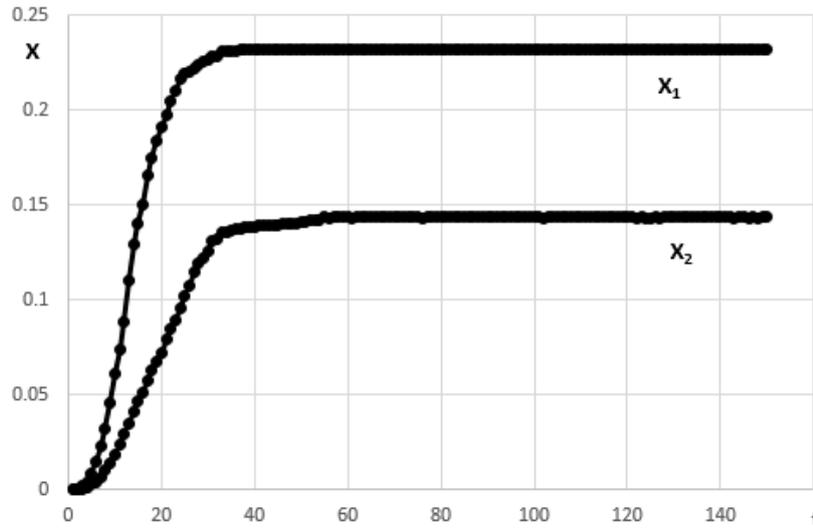


Fig. 1 – Time dependence of the crystallized fraction.

From Fig. 1, it can be seen that the time dependence of both volume fraction has a sigmoidal behaviour, typical for the Avrami equation [1–8, 15–17]. The main difference consists in the fact that the plateau values do not approach to unity as predicted in the original Avrami theory, but remaining to lower values. Moreover, we noticed that even their sum is smaller than 1. We explain this behaviour by the impingement effects between crystalline regions resulted from different polymer types. Due to these effects, a certain number of spherulites are blocked to increase their size and a considerable quantity of both polymers remains in the amorphous state. The effect is the same as in equation (4).

To prove this, employing a procedure similar to that we used in [15, 16], we rewrote our simulation program to work in two dimensions, in order to be able to plot a result comprising the situation of the spherulites towards the final stages of the simulation. In Fig. 2, we represent this type of situation for a square box with $L = 10$, $N_1 = N_2 = 100$, $\nu_1 = 0.06$ and $\nu_2 = 0.01$.

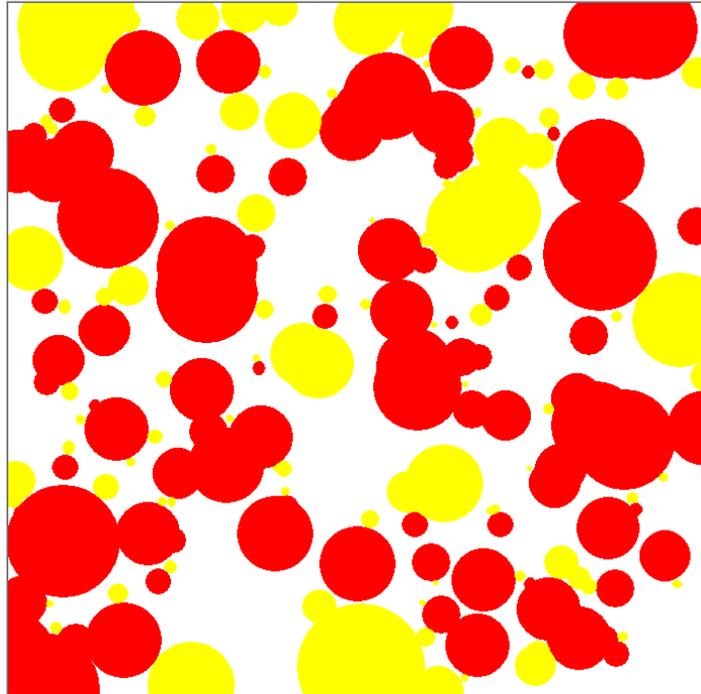


Fig. 2 – Final distribution of the spherulites for a 2-dimensional simulation.
The full color version may be accessed at <http://www.infim.ro/trp/>.

From Fig. 2, we notice that after reaching the maximum values of radii allowed by the impingement, there is a lot of empty space left (representing the amorphous state). We can also observe that the radius of spherulites is not the same as in the usual instantaneous crystallization, but we have a certain dispersion of them (as we already detected before).

Because the dependence on time of the crystalline fraction looks very similar with those obtained from the Avrami theory, we used equation (3) in order to check its validity. From the fraction of crystallized polymers recorded during simulations, we checked the dependence of $\ln[-\ln(1 - X_1)]$ and $\ln[-\ln(1 - X_2)]$ on $\ln t$.

Because the linear behaviour of these quantities on $\ln t$, we conclude that, especially at the beginning of the process, despite the impingement phenomena, the crystallization obeys the Avrami equation, as it is illustrated in Figs. 3 and 4.

The linear fit of the data gives for the Avrami index the values $n_1 = 2.983 \pm 0.003$ and $n_2 = 3.118 \pm 0.003$, which are in very good agreement with the predictions for the instantaneous nucleation in 3-dimensional space [5–8, 14–16].

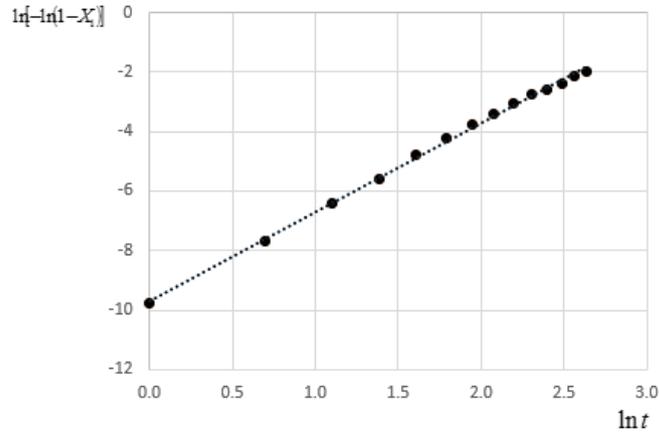


Fig. 3 – Representation of the equation (3) for the first polymer with $N_1 = 100$ and $v_1 = 0.06$. The dashed line is the linear fit of the data.

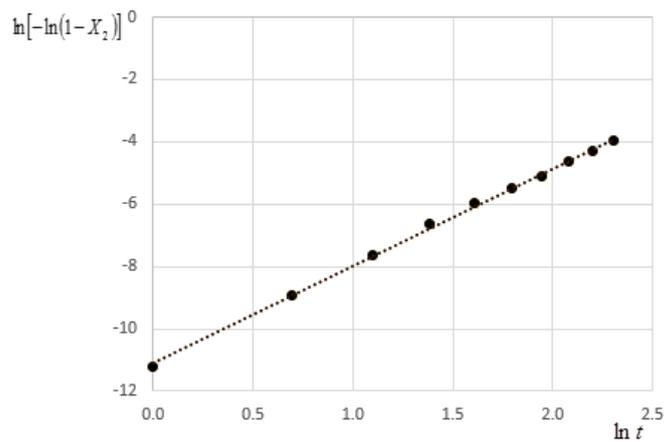


Fig. 4 – Representation of the equation (3) for the second polymer with $N_2 = 100$ and $v_2 = 0.04$. The dashed line is the linear fit of the data.

We repeated the simulations for symmetric polymeric blends with $N_1 = N_2 = 100$, but having different growth velocities. The results are summarized in Table 1 and confirm our assumption that, at least at the beginning of the nucleation process, the crystallizations obeys the Avrami model, because the Avrami index value is close to 3 (for all the considered velocities). We can explain this behaviour since at the beginning of the crystallization the nuclei are very small and they do not interact one with each other (therefore, the impingement is not so important to induce a clear deviation from the linear behaviour).

From Table 1, one can observe that the asymptotic values of the crystalline fractions with larger growth rates are higher. An explanation can be the fact that by increasing the radius of the species the free available space for the increase of the other dramatically drops.

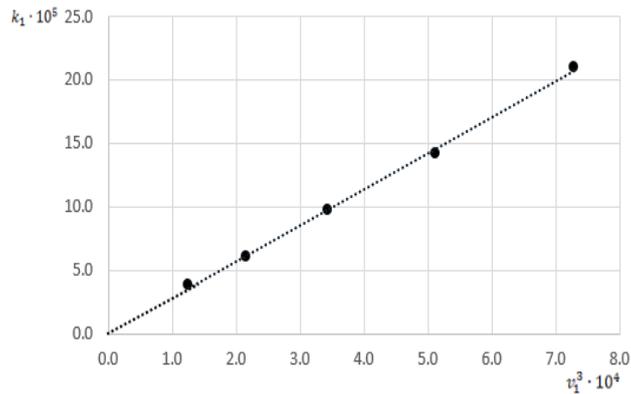
Table 1

Parameters of the Avrami equation obtained for simulations of symmetric polymeric blend with $N_1 = N_2 = 100$, at different growth velocities

v_1	v_2	n_1	n_2	$\ln k_1$	$\ln k_2$	$X_{\infty 1}$	$X_{\infty 2}$
0.09	0.01	2.977	2.907	-8.464	-14.762	0.413	0.038
0.08	0.02	2.983	3.069	-8.859	-13.006	0.367	0.103
0.07	0.03	2.986	3.036	-9.229	-11.777	0.296	0.133
0.06	0.04	2.983	3.118	-9.695	-11.094	0.232	0.143
0.05	0.05	2.955	3.070	-10.310	-10.351	0.202	0.190

Another important point is that the symmetric blend, $N_1 = N_2 = 100$ and $v_1 = v_2 = 0.05$, behaves almost like a homogeneous polymer, but with some impingement phenomena. This behaviour is supported for the tight values of the parameters from the Avrami equation and, especially, from the asymptotic values of the crystalline fractions.

We further investigated the Avrami-like behavior of the crystallization process by considering the dependence of the overall crystallization rate on the third power of the growth velocity for each species. The results are depicted in Fig. 5.



a)

Fig. 5

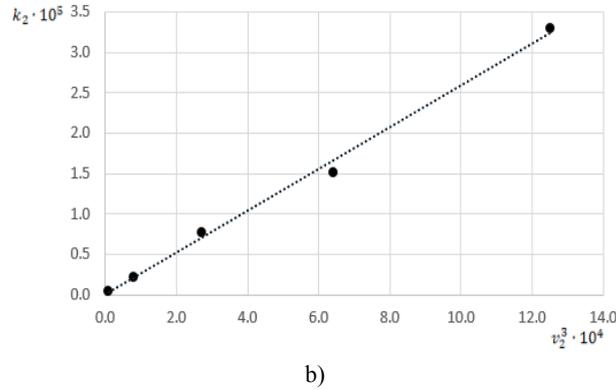


Fig. 5 (continued) – Dependence of the crystallization rate as function of third power of the growth velocity for the two species of the polymers. a) $0.05 \leq v_1 \leq 0.09$; b) $0.01 \leq v_2 \leq 0.05$.

The dashed lines are the linear fit of the data.

Both graphs are represented by straight lines passing through the origin, as equation (2) predicts, this being another confirmation that the process is ruled by the Avrami model.

3.2. INFLUENCE OF THE GROWTH VELOCITIES ON THE RADII DISTRIBUTION

As we already pointed out, due to the impingement, spherulites from the same polymer type do not have the same radii, as expected for the instantaneous nucleation. Therefore, we wish to find the distribution of the radii for the final volume of crystallization. In Fig. 6, we depict the histogram of the distribution of radii of the spherulites for an equimolecular system with $N_1 = N_2 = 100$ and growth velocities $v_1 = 0.07$ and $v_2 = 0.03$.

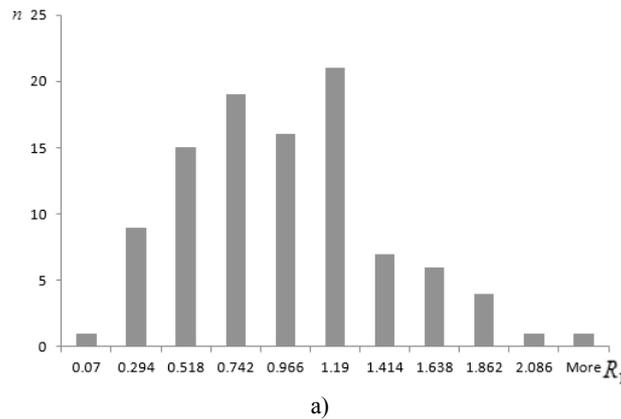


Fig. 6

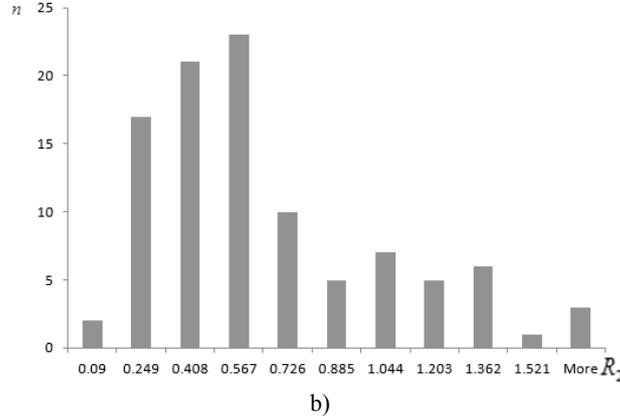


Fig. 6 (continued) – Radius of the spherulites for two growth velocities: a) $v_1 = 0.07$; b) $v_2 = 0.03$.

The histograms are relatively comparable, yet the one for the species having a higher growth velocity it is shifted towards larger values, as expected. The mean radius for $v_1 = 0.07$ is 0.855 ± 0.004 and for $v_2 = 0.03$ is 0.568 ± 0.004 , while the maximum radius is $R_1 = 1.190 \pm 0.005$ and $R_2 = 0.567 \pm 0.005$ respectively.

In the same time, the standard deviation for velocity $v_1 = 0.07$, $\sigma_1 = 0.4463$, is larger than for velocity $v_2 = 0.03$, $\sigma_2 = 0.3856$. In fact, by inspecting standard deviations for all data sets, we concluded that smaller growth velocities tend to minimize the spread of radii, this situation being very plausible by statistically point of view.

The results of the simulations for $L = 10$ and $N_1 = N_2 = 100$ are summarized in Table 2. We have to point out that the mean radius of the spherulites decreases as the growth velocity decreases.

Table 2

Radii statistics for simulations of symmetric polymeric blend with $N_1 = N_2 = 100$, at different growth velocities

v_1	v_2	\bar{R}_1	\bar{R}_2	σ_1	σ_2
0.09	0.01	1.0692	0.3234	0.4955	0.2262
0.08	0.02	0.9656	0.4822	0.4614	0.3466
0.07	0.03	0.8554	0.5688	0.4463	0.3856
0.06	0.04	0.7896	0.6476	0.4251	0.3961
0.05	0.05	0.7536	0.7240	0.2783	0.2127

The behaviour of the radii statistics also stands for the two dimensional case, confirming our observation that the Avrami equation has a universal behaviour, irrespective of the space dimensionality [15, 16].

3.3. THE ROLE OF THE CONCENTRATION OF NUCLEI

We made another set of simulations for a cubic box with $L = 10$, same growth velocities $v_1 = v_2 = 0.05$, but with a variable number of nuclei (however, keeping the total concentration constant). The main previous results remain, especially the time dependence of the volume fractions, which again obey the Avrami equation. The Avrami index is close to the value 3, as it is predicted for instantaneous nucleation [1–8, 15–17], with the observation that the behaviour is again valid, especially for the beginning of the nucleation process.

The results of the crystallization kinetics are summarized in Table 3.

Table 3

Parameters of the Avrami equation obtained for simulations at different nuclei concentrations and having equal growth velocities

N_1	N_2	n_1	n_2	$\ln k_1$	$\ln k_2$	$X_{\infty 1}$	$X_{\infty 2}$
150	50	3.057	3.012	-9.896	-10.923	0.579	0.050
140	60	3.1180	3.187	-10.029	-10.955	0.492	0.069
130	70	3.110	3.033	-10.101	-10.625	0.406	0.068
120	80	3.161	3.090	-10.235	-10.550	0.313	0.100
110	90	3.095	3.074	-10.264	-1.043	0.212	0.171
100	100	2.955	3.070	-10.310	-10.351	0.202	0.190

We also noticed that the asymptotic values of the volume fraction for the crystallized polymer are higher for larger concentrations, as it is somehow normal, while the difference increases with the ratio of concentrations.

We checked the dependence of the crystallization rate constants of both polymers on their corresponding nuclei concentrations. We found that the dependence is linear, as predicted by equation (2), but the results are more sensitive to the number of nuclei than to the velocity growth. For this reason, it is a necessity to perform a quite important number of simulations, especially for the unbalanced situations, where the difference in concentrations is large.

The statistics on radii reveals that the mean radius of the spherulites is always larger for the species with higher concentrations (difference that again increases for

the unbalanced melt). The results of the simulations for $L=10$ and $v_1 = v_2 = 0.05$ and different volume concentration of nuclei are summarized in Table 4.

Table 4

Radii statistics for simulations at constant nuclei growth
 $v_1 = v_2 = 0.05$ and different nuclei numbers

N_1	N_2	\bar{R}_1	\bar{R}_2	σ_1	σ_2
150	50	1.0666	0.5450	0.6281	0.2776
140	60	1.0360	0.5958	0.5861	0.2558
130	70	0.8600	0.5350	0.5701	0.2987
120	80	0.8437	0.6212	0.4549	0.3068
110	90	0.7583	0.6783	0.3931	0.3931

The spread of the radii is also larger for the polymer with a higher concentration ($\sigma_1 > \sigma_2$), the spherulites from the less abundant polymer being greatly hindered and thus being not able to increase to an extended radius domain.

4. CONCLUSIONS

In this paper, we report the Monte Carlo simulation results for a coincident instantaneous crystallization of a crystalline/crystalline binary polymer blend. During the runs, we took into account the impingement between spherulites from different polymers species, but we did not consider the impingement between spherulites from same polymers (as usual method [5–8, 14–16]).

Our computational model provided very good results and proves that, at least at the beginning of the process, both fractions of the crystalline polymers depend on time upon the Avrami equation.

From the simulation data, we obtained the Avrami index and the overall crystallization rate constant for both components.

We investigated the role of the crystallization velocity and concentration of the nuclei and, in all investigated situations, we found that the Avrami index is close to value 3, as it is predicted by theory of the instantaneous nucleation of polymers [7, 8]. Using a modified version of the simulation program, we also performed some tests for a 2-dimensional space and we found that the Avrami index is approximately 2.

The crystallization rate was found to depend on the third power of the growth velocity for each of the two polymeric species, as the theory forecasts for regular instantaneous nucleation processes.

The simulations for the planar situations showed that, after reaching the maximum values of radii allowed by the impingement, always remains some empty space that is equivalent with the amorphous state. These observations explain that the asymptotic values of the crystalline fractions are much smaller than unity, even their sum staying below value 1.

Another interesting result is that the radius of spherulites is not the same as in the usual instantaneous crystallization, but we get a dispersion of the radii for both polymeric species. This behaviour is explained being as a direct effect of the impingement phenomena and therefore we performed a thorough statistical investigation of the distribution of the spherulites' radii.

The key conclusion for this kind of crystallization of blend polymers is that the Avrami theory is an universal instrument that can be used to describe the nucleation process.

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