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Cellular Automata Simulation of Dissipative Structure Formation in Heterogeneous Polymer Systems, Formation of Networks of a Dispersed Phase by Flocculation

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Abstract. — Dissipative structures are responsible for many non-linear property changes in heterogeneous polymer systems, as has been shown experimentally [1] and theoretically [2]. Using the "cellular automata" program it was possible for the first time to simulate the formation of the complex network structures formed by a complex flocculation process from dispersed particles or phases. The simulation results lead to some interesting conclusions for the behaviour of the real systems.

1. Introduction

The properties (conductivity, impact strength) of heterogeneous polymer systems are preferably being described with the help of the "percolation theory". Its popularity is based on the simplistic assumption, that particles (or phases) are statistically dispersed in the polymeric matrix, during dispersion or compounding, which has never been shown to be the case.

In reality the contrary is the case [1]. In the past 15 years I have worked experimentally [1] and theoretically [2] on understanding and describing the dynamics in heterogeneous polymer (and other colloidal) [3] systems, which are responsible for the special phenomena like conductivity (when the dispersed phase is a conductive phase), or impact resistance above certain critical concentration values, viscosity or gel formation [3]. This interest was raised by the general lack of understanding in the polymer field how real polymer systems (plastics, compounds, masterbatches) behave. It was possible to show that their properties are due to the non-equilibrium character of such colloidal systems, and to the fact, that above certain overcritical amounts of (dispersion) energy input the "dissipative structures" [4] are being formed [1]. In polymer systems these are networks of formerly fully dispersed, then flocculated, particles or phases with a joint adsorbed layer of matrix polymer molecules like a snake-skin [1].

It was shown [1–3], that the "percolation theory" is not an appropriate tool to describe such phenomena like the sudden conductivity break-through above the critical concentration, although this theory is still very popular. Part of the popularity of this theory is due to its

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simple simulation on a computer, by using a program which places dots on a 2D screen on
places only based on statistical rules [5].

Instead of the unrealistic percolation model, the present paper investigates a simple cellular
automata simulation for these polymer systems. It is important to understand, that it is meant
to describe non-equilibrium phenomena on the mesoscopic scale - the behaviour of phases in a
size range between 10 nm and 1 μ. There is one other simulation [6] devoted to the mesoscopic
range, but this one tries to describe diffusion controlled change of a stable colloidal system to
a precipitating suspension, a process directed towards thermodynamical equilibrium. Many
other simulations are oriented to the molecular scale and cannot be used for our purpose here
either.

2. Experimental Basis

The process of the formation of flocculated networks of dispersed particles or phases in hetero-
geneous polymer systems consists of various elements [1,2], which are necessary to understand
before looking at the simulations:

1. dispersion is the step during which the particle (or phase) is forced to be wetted by a
monomolecular, firmly adsorbed layer of matrix molecules under melt fracture conditions,
(whereby the formerly adsorbed layer of gas and water is desorbed)

2. the dispersed particles with their new shell are not statistically distributed throughout the
whole matrix but they assemble in monolayers (“seams”), which penetrate the polymer
system like coal seams do the earth or like veins do the body

3. above a thermodynamically well-defined [2] critical concentration, when the “slam” is full
of dispersed particles, they lose part of their adsorbed shell, so that they can approach
each other closer, and form a joint adsorbed layer, which, after more flocculation steps,
takes the form of an elastic tube (or snake skin) with golfballs incorporated.

The particles are generally 50 to 200 nm small, the adsorbed layer is about 20 nm thick, so
that dispersed particles have a diameter of 90 to 240 nm.

Figures 1 and 2 are showing the schematics of this process, Figures 3 and 4 the most impres-
sive scanning electron microscope pictures showing these networks of dispersed and flocculated
particles in a polystyrene compound at the critical concentration [1].

A program capable of simulating the network formation – taking into account the experi-
mental facts - must therefore reflect

• the interaction of particles (something happens, if particles are contacting).

• the dynamics of the process (“flocculation occurs, if ... , does not occur, if ... ”),

• the representation of single-particle membered chains in the network (not just a net-
work of whatever chain thickness), leading to a chain diameter of about 100 to 250 nm
thickness),

• the formation of branched chains which join to form a net.

• certain stability criteria (“redispersion or degradation of the network occurs, if ... ”)

and must account for the fact, that these structures are highly stable when subjected to
annealing - they are situated in an energy valley placed very high on top of the non-equilibrium
energy mountain.
Fig. 1. — Proposed flocculation mechanism for “brittle-to-tough-transition” in polymer blends [2c]; it is similar to the mechanism in conductive compounds or blends, where the particles do not fuse (last step does not occur in the latter systems [1]).

The program “cellular automata”, available as an interactive demo program version [7] proved to be useful as a first step into simulating this structure formation. The automata used in the demonstration are based on two-state models (like: sites are “occupied” or “vacant”, or: cells are “alive” or “dead”) that obey totalistic rules involving nearest neighbours. This program is often used for simulation of biological growth or evolution processes, which are also of non-equilibrium character and highly dynamic. It is capable of describing self-organized criticality.

So it makes sense to use this program with the following understanding:

- sites in black are understood to be “flocculated particles”, those in white are called “dispersed particles”

- one site is representing one particle with a size of about 100 to 250 nm

- the 2D screen is appropriate because the dispersed phases aggregate and flocculate in flat monolayers (“seams”), in principle in 2 dimensions

- in reality particles (phases) can only flocculate when the “seam” is full and the flocculating particles are in close contact.
Fig. 2. — Flocculated particles forming chains [8].

Fig. 3. — SEM-picture of break surface in a carbon black compound with a concentration at the flocculation point (6%) [1].
The only problem for performing the simulation was to find the rules for when sites are to be called "flocculated" or "dispersed". The program allows for about 250,000 different rules, one of which is described with the notation $[-4678, +35678]$ which means: "cells become alive, if there are 4, 6, 7 or 8 alive neighbours; a living cell will stay alive, if it has 3, 5, 6, 7 or 8 living neighbours". We could also say for our simulation goal here: "A dispersed particle will flocculate, if it has 4, 6, 7 or 8 neighbours; it will stay in the flocculated stage, if it has 3, 5, 6, 7 or 8 flocculated neighbours. "It also leads to some kind of network (Fig. 5); but this network has a (chain) diameter of different "cell" or "particles" number and a varying thickness. This is not a correct representation of the dissipative structures found in heterogeneous polymer systems, when particles flocculate to networks of branched chains.

3. Results

Every simulation experiment was started with a statistical distribution of black and white dots. The interaction of a site ("particle") with 8 neighbours was used.

Several rules like $[-234, +2]$, $[-234, +23]$ and $[-347, +23]$ are resulting in nice networks in the 2nd or 3rd iteration step. These rules and many others were tried based on the idea that a dispersed particle will flocculate if it has 2, 3, 4 or more tightly touching, flocculated particles (which proved to be helpful), and a flocculated chain will survive in this form when one flocculated particle has 2 or 3 flocculated neighbours (I first believed, that the branching would only occur and survive, if the survival rule contained the parameter "3". This showed to be wrong, because such partially very nice chain networks are unstable and will form either irregular structures or stable "circles" in the following iteration steps.) Because I only accepted results which were stable over many dozens of iteration steps, I had to change the basic assumptions.

Only when the rule was changed to $[-234, +12]$ not only branched chains and continuous networks were formed, but these were also stable over many (and probably infinite) numbers
Fig. 5. — "Wrong" network structure using \([-4678, +35678]\).
The surprise (at least to me) was the necessity of introducing the "1" as a parameter in the survival rule (a flocculated particle remains flocculated, if it has 1 flocculated neighbour), but not in the formation rule. The "1" tells us, that flocculating chains are able to grow, which we have to expect from experimental results. And finally I am not using a "3" in the survival rule although I first expected that only then branching would become stable (the reader may also try [-234, +123] and will see that it is not successful). With the above mentioned notation a dynamic network is created, i.e., that under conditions where some flow may occur the flocculation is dynamic, always changing its shape and specific form - which I believe is a correct representation of the real processes.

Fig. 6. — Simulation run using [-234, +12], showing 3 iteration steps in sequence.
Fig. 7. — Simulation run using $[-234, +12]$, showing 3 iteration steps in sequence.

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Fig. 8. — Simulation run using $[-234, +12]$, showing 4 iteration steps in sequence.

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