Applied Mathematical Modelling 51 (2017) 109–128

Contents lists available at ScienceDirect

Applied Mathematical Modelling

journal homepage: www.elsevier.com/locate/apm

Associations and dissociations with time-dependent reaction coefficients in finite polymer mixtures: The model and analytical-numerical method for solution by successive approximations

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ARTICLE INFO

Article history:
Received 22 March 2014
Revised 20 March 2017
Accepted 20 April 2017
Available online 8 June 2017

Keywords:
Homopolymer mixture
Chemical reaction with time-dependent coefficients
Quadratic ordinary differential equation
Discrete Smoluchowski model
Analytical-numerical method
Steady-state solution

ABSTRACT

The work deals with the association and dissociation reactions with time-dependent coefficients in finite mixtures of polymers dispersed in fluid media with solid components. The polymers are regarded to be formed by identical units, polymer-forming units (PFUs) and, thus, present homopolymers. The model takes into account the porosity of the dispersion-medium/polymer-mixture system. The work derives the model for the reactions in the finite mixtures. The model presents a non-autonomous quadratic finite ODE system in a time-independent hyperplane and is based on the conservation law for the total number of PFUs. A variety of engineering applications of the derived finite-mixture model are discussed. The simplest case of the finite mixtures, i.e., the monomer-dimer mixtures with time-independent reaction coefficients is completely analyzed. An analytical-numerical (AN) method of the successive-approximations (SA) type is proposed for solving the derived model. The AN/SA method includes explicit analytical expressions for each of the approximations in terms of the preceding approximation. The method is exact in the dissociation-only case. The approximations are expected to converge if the association-reaction coefficients are not too large and the zeroth approximations are not very far from the solution. The AN/SA method comprises two sequences of the approximations. If the first one converges uniformly in the entire time axis, then the limit function is a steady-state (or "dynamic equilibrium") solution of the non-autonomous quadratic ODE system. The second sequence presumes that the first sequence is convergent in the above mentioned sense. The second sequence is intended for calculation of the solutions of initial-value problems for the above ODE system in a semi-infinite time interval. The main differences from common computational methods are formulated. The AN/SA method is quantitatively illustrated with a few examples of the settings in the aforementioned case of monomer-dimer mixtures, also in comparison with the explicit Euler method. The form of the AN/SA method allows especially efficient implementation on multi-processor/multi-

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http://dx.doi.org/10.1016/j.apm.2017.04.022

core personal computers with graphic processing units even if the dimension of the state space is large. The developed model and method form a constructive framework for analysis or design of polymer mixtures dispersed in fluid-solid media. An application to prospective manufacturing of spatially heterogeneous polymer products is noted. A few directions for future research are proposed as well.

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1. Introduction

Physics, Chemistry, and engineering deal with various complex systems. Along with this, there are systems, which are in a certain sense, much more complex. For instance [1, p. C49]:

> *Biological systems are very different from the physical or chemical systems analyzed by statistical mechanics or hydrodynamics. Statistical mechanics typically deals with systems containing many copies of a few interacting components, whereas cells contain from a million to a few copies of each of thousands of different components, each with very specific interactions.*

One of the well-known examples of the systems with a large number of the components is a mixture of polymers. By polymers, we understand particles composed of specific numbers of identical elementary units, e.g., atoms or molecules. Strictly speaking, such polymers are called homopolymers.

The study of the association of such polymers was initiated by Smoluchowski who wrote down an equation for the association of particles [2]. The equation contains kernels that multiply the concentrations in quadratic forms to describe the time development of the concentrations. Smoluchowski solved the equations for the special case of constant kernels [3]. Apart from the constant kernels, the treatment was also approximate because the equations only included terms that describe association and no dissociation of the formed particles is possible, i.e., the reactions were considered irreversible. It was later realized, still within the description of the elementary processes as irreversible, that for other choices of the kernels, the equations can give rise to gelling, i.e., a process where monomers associate into an infinite size polymer in a finite time [4]. Kernels that can give rise to gelling transitions include those that resemble the chemically relevant polymerization processes that produce, for example, technologically important plastics. These result was later extended to reversible cases [5].

Other solutions in closed forms have been given for several types of kernels, beyond the solution given by Smoluchowski. They include kernels on the form $i + j$ and $i\,j$ where i and j are the sizes of the reacting polymers [6,7] (see also the review in [8] for a summary of the state of the art around the turn of the millennium).

Importantly, it was established that solutions of both the irreversible and reversible association equation will under some circumstances scale. This scaling also holds for the kernels that cause a gelling transition [9,10]. For irreversible association, in particular, the scaling means that the polymer size distribution will be given by a single parameter. This can be chosen as the average size.

Most of these results have been derived for explicitly defined kernels or kernels with certain properties, e.g., being harmonic functions. The limited number of kernels for which exact solutions are known shows that the solution of the more general problem with time and position dependent coefficients, in addition to size dependent values, is a rather complicated problem. The present work aims at extending procedures for solutions of the equations where the kernels are time dependent.

Polymers can also be composed by a few types of units (e.g., [11, Section 4.3]). In this case, polymers are known as copolymers. In particular, copolymers present most of the molecules typical in biological systems. Moreover, all biochemical transformations are fundamentally unimolecular or bimolecular (e.g., [12, the left column on p. 171/2]), similarly to reactions in homopolymer systems. One of the examples of copolymers in biological systems is illustrated with biochemical reactions of intracellular molecules (e.g., [13]).

The present work considers homopolymers only. They are for brevity referred as polymers. Physical aspects of various polymer mixtures are reviewed, e.g., in [14].

A mixture of polymers contains j-mers at values of j in set $\mathbb{N} = 1, 2, 3, \ldots$, i.e., monomers, dimers, trimers, tetramers, and so on. A j-mer consists of j units. For this reason, we call j the size of a j-mer. Let parameters υ and m such that

$$0 \le \upsilon < \infty \tag{1.1}$$

and $0 < m < \infty$ be the volume and mass of the unit. The present work assumes that they are independent of the sizes of the polymers. Then the volume and mass of a j-mer are υj and mj, respectively.

In general, at any fixed j, j-mers may differ from each other in their shapes and structures. Following a number of other works on the topic, we assume that, at any j fixed, all j-mers are identical. Thus, a polymer mixture can be regarded as a population of the polymer-forming units (PFUs), which is subdivided into a number of components in such a way that, at any fixed j, the jth component consists of identical j-mers.