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Chitosan-based polymer electrolyte films to culture fractals and the simulation of multiple cluster fractal patterns

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ABSTRACT

Besides various applications in electrochemical devices, polymer electrolyte films such as Chitosan have the potential of being media to culture fractals. In the authors' laboratory, dendritic growth has been observed in these films. Similar findings have proven that these types of dendritic growth may be of fractal-like growth patterns. There have been many simulation works of fractal growth patterns of single cluster fractal patterns. Yet, attempts to simulate multiple cluster fractal patterns such as found in these films are very few and may have not been done. For the first time, a simulation of multiple cluster fractal growth patterns in polymer electrolyte films is done by adopting the fractal theory and Diffusion limited aggregation (DLA) model incorporating fractal growth parameters that includes sticking coefficient, number of particles and different lattice sites. The fractal dimensions, D of the fractal patterns obtained from experimental and simulation work were calculated using the box-counting method. Variations of simulation parameters of fractal clusters and fractal dimensions are investigated. Fractal dimension analyses of the original fractals observed in the polymer electrolyte films and the simulated fractal patterns provide better understanding of the formation of these fractal growth patterns.

1. Introduction

An electrolyte is a substance containing free ions that behaves as an electrically conductive medium. Because they generally consist of ions in solution, electrolytes are also known as ionic solutions, but molten electrolytes and solid electrolytes are also possible. Polymers, electrical non-conducting substances, can become ionically conducting when inorganic salts are infused in them. The polymers act as a host while the inorganic salts dissociate in them to provide the ions necessary for conduction. These ionic conducting polymers are known as polymer electrolytes. In this work, Chitosan-based polymer electrolyte films were used to culture fractals.Usually, research works on fractals were done only on laboratory experiments, theoretical modeling and experimental studies, or modeling and computer simulations. Recently, integration of all the three approaches; experimental, modeling and simulation have been reported by Amir et al. (2010, 2011a, 2011b). However, these works were only concentrated on the study of single cluster fractal growth patterns without the inclusion of other fractal growth parameters such as sticking coefficients and different lattice sites. In the present work, attention is given on finding the passé-part out of the study of such fractal growth patterns by addition of the other fractal growth parameters carried out for multiple clusters of fractal growth patterns. Further understanding on the formation of such aggregates can be achieved with the introduction of the fractal growth parameters as mentioned above.

Theoretical simulation of fractal patterns, in particular Diffusion Limited Aggregates (DLA) requires particles, uniform as well as non-uniform, performing random walk (Witten and Sander, 1981). On approaching the nucleation center (seed), these random walker stick to it and form an aggregate leading to DLAs of different size and varying dimensionality. To obtain such patterns in laboratory framework, systems with particles in random walk that subsequently form aggregates are required. As reported by Hashim et al. (2000), dissociated free ions in polymer electrolytes can perform random walk to form large size DLA patterns.

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2. Experimental

Chitosan-silver nitrate ($AgNO_3$) films were prepared by dissolving 1 g chitosan (mol wt. ~3.1×10^5) and $AgNO_3$ in 100 ml of 1% acetic acid solutions. Chitosan polymer electrolyte films were prepared using solution casting method. The mixtures were stirred for about 10-12 hours. Each solution that has completely dissolved was then cast into petri dishes (~10 cm dia.) and left to dry slowly at room temperature in a dark and dry place for several weeks.

3. Theoretical Simulation Model

DLA is a phenomenon that is observed in many areas of nature, ranging from physics to geology to chemistry to biology to meteorology. Random fractal growth processes essential condition can be described by DLA model. The model is set by the following simple rules:

A seed is fixed at the origin of some coordinate system and one particle is released from a far-away boundary and allowed to take random walks (diffuse). If the particle touches the seed, it irreversibly sticks to the seed and forms a two-particle aggregate. As soon as the random walker is removed either by being captured or escaping the boundary, the next walker is released and the process is repeated. This new walker can stick to any particle in the aggregate as well as seed particle.

As there are lots of models in the field of investigation of fractals, computation is a way to compare the nature with the models. For DLA-cluster one approach is to simulate the random walk of the particles and their aggregation. Typically one uses a lattice, puts an initial seed particle at some origin and another particle somewhere on the lattice. Then the second particle moves around in random motion, step by step from lattice site to lattice site. Finally it will meet the first particle. Then another particle is thrown onto the lattice, it walks around and after a while meets the first two. This is continued for as many particles as one likes, one after the other (Witten and Sander, 1983) DLA model.

In this work, the simulation work involved devising computer programming for simulation of multiple cluster fractals. In this program, important aspects of fractal formation parameters were implemented according to the suitability of the fractal patterns being simulated. Computer simulations were performed on the platform of MATLAB Version 7.12 (R2011a). MATLAB was chosen as it allows matrix manipulations, plotting of functions and data, implementation of algorithms, creation of user interfaces, and interfacing with programs written in other programming languages, including C, C++, Java, and Fortran. It can solve technical computing problems faster than traditional programming languages. Apart from that, MATLAB also provides MATLAB Compiler Runtime (MCR) used for simplifying distribution of compiled applications and components.

In the simulation of multiple cluster fractals, one important feature is the ability to run fractal growth of multiple seeds by implementing nucleation centers (seed) randomly within an area with a specific radius, R that can accommodate large number of particles, M. The aim of this simulation is to replicate the growth of multiple cluster fractal growth pattern observed in the cultured fractals. For that purpose, a simulation program of multiple cluster fractal growth patterns has been successfully developed and the results are found to be quite interesting to study.

4. Results and discussions

In the present work, fractals were obtained in laboratory conditions using solid polymer electrolyte films as the media of growth. Chitosan-$AgNO_3$ polymer electrolyte films were prepared via solution casting method. In the particular system, the movement of the ions (anions and cations) from the inorganic salt was expected. The formation of fractals is believed to be due to the ions from the inorganic salt performing random walks and their subsequent sticking (Chandra, 1996; Chattaraj et al., 1996; Somasundaran, 2003). The important experimental feature is that no external bias was necessary for either the creation or subsequent aggregation of the 'random walkers/ions' as done in the electrode position systems (Chandra, 1996).

Digital photos of the experimentally cultured fractals were taken, pre-processed via image processing software and uploaded to a fractal dimension determination software tool developed specifically in our laboratory. Fig. 1 shows the experimentally cultured fractals of chitosan-$AgNO_3$ polymer electrolyte film. As can be observed in the figure, fractals formed at different nucleation centers and then grew in the direction away from the nucleation sites. The fractals grew irregularly and in an unpredictable motion which can be attributed to the Brownian motion of aggregating species. The different sizes and shapes of these fractals are due to the occurrence of other nucleation sites. The fractals do not overlap each other but are separated from each other by a definite boundary.

In the simulation of multiple cluster fractal growth patterns, one important feature is the ability to run fractal growth of multiple seeds simultaneously by implementing nucleation centers (seed) randomly within an area with a specific radius, R that can accommodate large number of particles, M. The aim of this simulation is to replicate the growth of multiple cluster fractal growth pattern observed in the cultured fractals. For that purpose, a simulation program of multiple cluster fractal growth patterns has been successfully developed.

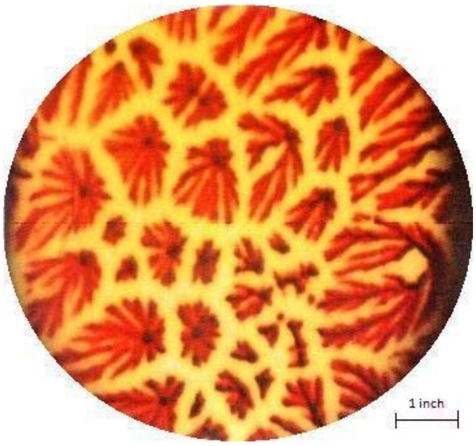


Fig. 1: DLA fractal of chitosan-$AgNO_3$ cultured in the authors' laboratory

The cultured fractals of chitosan-$AgNO_3$ polymer electrolyte film exhibit multiple cluster fractal growth patterns that form within areas where the number of clusters depend on the number of nucleation sites (seeds). From close observation, in these areas, there consist of big and small clusters together in a group of mainly five clusters. In Fig. 1, the chitosan-$AgNO_3$ polymer electrolyte film roughly has about 30 visible clusters. Most of the clusters within the films are found to be scattered and do not overlap each other (Fig. 2).

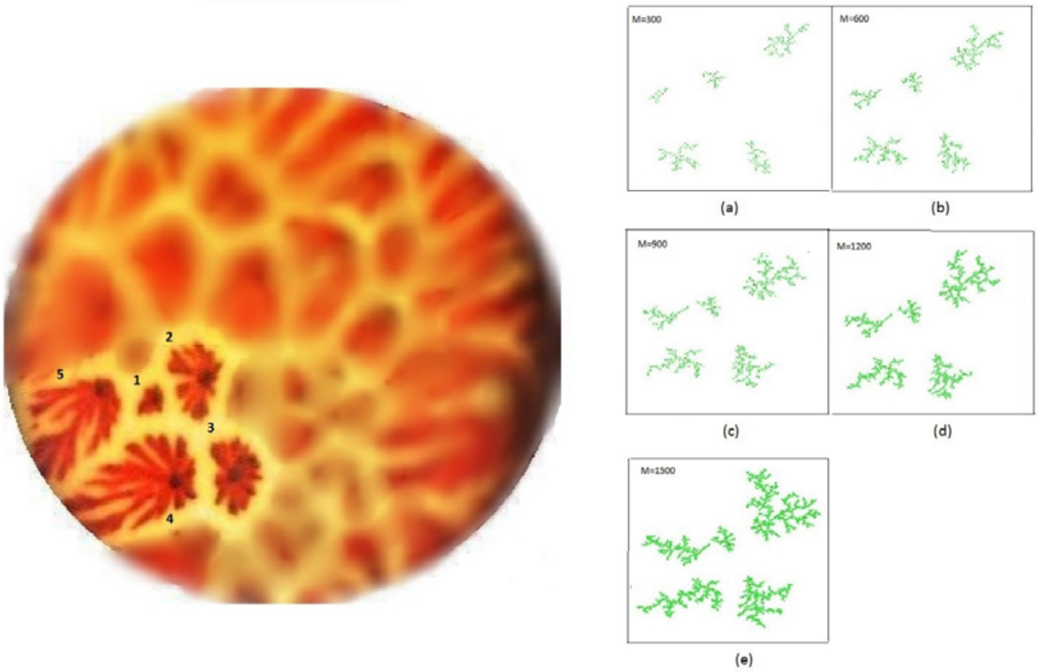
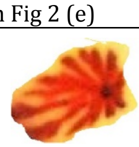
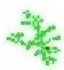
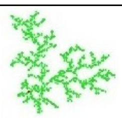


Fig. 2: Simulation of a region of multiple cluster fractal growth patterns observed in the cultured chitosan-$AgNO_3$ polymer electrolyte film with 5 seeds

With this consideration, the simulation of multiple cluster growth patterns was done by varying the number of seeds representing clusters contain within certain areas and the whole film. For the simulation of the multiple cluster fractal growth patterns in the chitosan-$AgNO_3$ polymer electrolyte film, the prescribed parameters are M=1500 particles with sticking coefficient of 0.7 and 8 lattice sites. Fig. 2(a) - (e) shows the stages of simulation at 300, 600, 900, 1200 and 1500 particles respectively of a region consisting of multiple cluster fractals with 5 nucleation sites as seen in the film of chitosan-$AgNO_3$ labelled 1-5 clock-wise. For the multiple cluster simulation shown in Fig. 2, fractal dimension values of each of the cultured and simulated fractal patterns are tabulated in Table 1.

Table 1: Fractal dimension values of each of the cultured and simulated fractal patterns for the multiple cluster simulation at the final stage of growth of M=1500 particles as shown in Fig 2 (e)

Cultured fractals of clusters 1-5 from left to right					
Fractal dimension	1.5943± 0.054	1.6585± 0.047	1.6657 ± 0.049	1.6246± 0.048	1.6734± 0.045
Simulated Fig by each cluster					
Fractal dimension	1.6486± 0.052	1.6798± 0.042	1.6563 ± 0.051	1.6094± 0.045	1.6593± 0.049

To get suitable images of fractal patterns for simulation, the process of culturing fractals in the laboratory was carefully executed. The table shows that the fractal dimension values of the simulated fractals are comparable with the fractal dimension values obtained from their respective experimentally cultured ones. For example, the fractal dimension of the experimentally cultured fractal clusters 4 and 5 in Fig. 2 are 1.6246 ± 0.048 and 1.6734 ± 0.045, while the fractal dimension values for their simulated patterns are 1.6094 ± 0.045 and 1.6593 ± 0.049 respectively. These show that the simulated fractal patterns were comparable to the results of similar polymer electrolyte films as done by Suraiya Begum et al. (2016) of fairly good conformity with the fractal patterns observed in the chitosan-$AgNO_3$ polymer films.

For every type of cultured fractals, the size, shape and density of particles are found to be different. Thus by implementing simulation of different parameters facilitates more efficient way of getting better comparison between the simulated and cultured fractal growth pattern. By making this comparison, the understanding on how such fractal growth patterns occur can further be enhanced. It can be averred that for smaller size of any single cluster, smaller values of max particles should be applied in the simulation. Generally, shape of a cluster with more lattice sites tends to give a more compact look and the higher sticking coefficient presents a denser appearance.

5. Conclusions

The emergence of dendritic growth patterns identified as fractals in the polymer electrolyte films, proved that besides applications in electrochemical devices, polymer electrolyte films are also suitable for the study of fractals. Study of the growth of these fractal patterns has been carried out using the simulation based on the DLA model. The simulation technique chosen has the capability of producing images with fractal dimension values comparable with those obtained for experimentally observed fractals. Moreover, the instauration of the sticking coefficient along with different numbers of lattice sites for multiple cluster fractal pattern simulations, have shown that simulation of the multiple cluster fractal patterns can be applied accordingly. This indicates that the computer program undertaking the DLA model has successfully come out with outputs that are in accordance with the original patterns found in the chitosan-$AgNO_3$ polymer electrolyte films.

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References

Amir S, Ali SH and Mohamed NS (2011b). Implementation of a diffusion-limited aggregation model in the simulation of fractals in PVDF-HFP/PEMA–NH4CF3SO3–Cr2O3 nanocomposite polymer electrolyte films. Physica Scripta, 84(4): 045802.

Amir S, Hashim_Ali SA and Mohamed NSB (2011a). Studies of fractal growth patterns in poly (ethylene oxide) and chitosan membranes. Ionics, 17(2):121-125.

Amir S, Mohamed N and Hashim AS (2010). Simulation model of the fractal patterns in ionic conducting polymer films. Open Physics, 8(1): 150-156.

Begum SS, Aswal VK & Ramasamy RP (2016). Small Angle Neutron Scattering and Spectroscopic Investigations of Ag Fractal Formation in Chitosan-Ag Nanocomposite Facilitated by Hydrazine Hydrate. The Journal of Physical Chemistry C. 120 (4): 2400-2410.

Chandra A (1996). Anion clustering and fractal pattern growth in ion conducting polymeric matrix. Solid state ionics, 86(8): 1437-1442.

Chattaraj PP, Kalidaha AK, Mukhopadhyay R, Bhattacharya AK and Tripathy DK (1996). Rheological study of filled SBR compounds with trans-polyoctenylene (TOR) and their interaction mechanism. International Journal of Polymeric Materials, 33(1-2): 73-87.

Hashim AS, Mohamed NSSAA and Arof AK (2000). Solid state ionic devices: Science and Technology. Allied publishers Limited, Chennai, India.

Somasundaran P and Runkana V (2003). Modeling flocculation of colloidal mineral suspensions using population balances. International Journal of Mineral Processing, 72(1): 33-55.

Witten TA & Sander LM (1981). Diffusion-limited aggregation, a kinetic critical phenomenon. Physical Review Letters, 47(19): 1400-1403.

Witten TA & Sander LM (1983). Diffusion-limited aggregation. Physical Review B, 27(9): 5686-5697.