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Research Article

Diffusion-Limited Aggregation in Potato Starch and Hydrogen Borate Electrolyte System

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Natural growth of diffusion-limited aggregate (DLA), without any external stimuli, in boric acid doped starch system is reported here. Fractals grown were confirmed to be of diffusion-limited aggregate (DLA) pattern having fractal dimension ~1.49. Effect of substrate and humidity on growth pattern has also been discussed. The existence of a different vibration band of H_3BO_3 in FTIR confirmed that growth structures are related to boric acid. XRD pattern has shown broad peak along with some sharp peaks. Broad peak is related to starch's amorphous nature, as where intense sharp peaks are due to boric acid.

1. Introduction

Nature prefers symmetry. Mountains, snowflakes, branches of trees, shores of continent, and so forth are some visible examples of symmetrical structures in nature. More patterns of self-similar structures encountered with mankind are cancer, piles, and so forth. Retinal circulation of the normal human retinal vasculature is, also, statistically self-similar and fractal. Hence fractals are one of the most important topics in biology and medicinal field which generally covers the study of (a) the understanding of spatial shape and branching structure, and (b) the analysis of time varying signal. By knowing the branching structures of tissues and organs, biologists use this to discriminate between normal and pathological structures.

This has made the growth phenomenon of complex structure an interesting area of research for a long time [1–11]. Several models have been presented to understand the phenomena out of which diffusion limited aggregation model had received much attention as this is very common in nature [12–14]. Fractals are self-similar objects with non integer dimension; they are also important to determine the macroscopic properties of the system by microscopic dynamics of system, which has been an area of scientific interest for a long time. Electrodeposition, chemical dissolution, electrical breakdown, and chemical redox reaction are all the examples of experimentally observed fractals.

Under external stimuli, transport properties of dispersed and mixed ion conductors are studied using percolation theory along with fractal concept. It is supposed that clusters of molecules are randomly formed in solution and attached to each other. At saturation, clusters are large enough to nucleate and then grow on their own or other solid surfaces. For ion transport polymer matrix is supposed to have flexibility comparable to liquid systems. Considering this fact, polymer electrolytes were recognized as ideal frameworks for the developing of fractal structure due to presence of random walks of free ions, if the walking species has aggregating tendency [15–17], literature shows the growth of boric acid crystals and formation of clusters of various shapes and sizes [18–20]. Hence, it has been planned to study fractal growing phenomenon in starch doped boric acid systems.

In present study large size (2-3 cm) fractal growth without any external stimuli has been investigated. The structure is due to boric acid clusters which are confirmed by the presence of intense hydrogen borate peaks in XRD analysis as well

as FTIR spectroscopy. Possible chemical structure has been proposed for the system. SEM has been used to reveal the surface morphology.

2. Experimental

2.1. Sample Preparation. Potato starch (PS) $(C_6H_{10}O_5)_n$ (Loba Chemie), H_3BO_3 (Anchor Laboratories), Glutaraldehyde (GA) $(C_5H_8O_2)$ (Loba Chemie) and distilled water (as a solvent) was used in the study. Materials were used as received. GA is added in the system; Samples have been prepared using solution cast technique at 30°C. For 1 gm of starch, 0.3 gm H_3BO_3 and 2 mL GA water were taken together in 10 mL of solvent, mixture was stirred at 30°C on magnetic stirrer for one hour and heated till it dries. Samples were then left in atmosphere to dry at room temperature ~20–24°C. Within one week fractals were visible.

2.2. Devices and Technique. Optical photographs of the samples were taken by Sony Cybershot (DSC-S730), and for optical micrograph camera Catalyst biotech CC130 is used. IR spectral studies have been carried out, by Jasco FT/IR 5300, to confirm the complexation. SEM micrographs have been taken using JEOL JXA 8100 Electron Probe Micro-analyser. Philips X-pert model with CuK_α (λ = 1.542 Å) is used for XRD study. Crystallite size (D) and microstrain (ξ) have been calculated using Scherrer's semiempirical formula

$$D = 0.9\frac{\lambda}{\beta\cos\theta}, \qquad \xi = \frac{\beta}{4\tan\theta}, \tag{1}$$

where β is the full width half maxima of the highest intensity peak, and λ is the CuK_α wavelength = 1.54 Å.

3. Result and Discussion

3.1. Computation of Fractal Dimension. Optical photograph of the fractal is shown in Figure 1(a), while close view of the ramified structure is given in Figures 1(b) and 1(c).

The microscopic views 1(b), and 1(c) of the growth structure indicates, growth is starting from a seed; on growing it is divided into branches; no two tips are touching each other; they are changing their pathways by bending when they reach to be very close to each other or the growth stops there.

All these observations are indicating that the pattern of growth is of the DLA type, which is further confirmed by fractal dimension.

Fractal dimension has been calculated by extracting the data from the real picture 1(b) using software "xyExtract." The extracted image of the pattern is given in Figure 2.

There are different methods for calculating fractal dimension "d_f", for example, box counting method [21, 22], mass radius relation [23] scaling relation of two-point density-density correlation function [24]. We have calculated the fractal dimension by calculating filled area [25], and the formula used in calculation is

$$d_f = \frac{\log\left[M\left(\mathrm{NL}\right)/M\left(L\right)\right]}{\log N}, \tag{2}$$

where L represents the unit length, N is the number of unit length, M(NL) is the filled area of a square of length NL, and $M(L)$ is the filled area of a square of unit length. Fractal dimension calculated by this is found to be 1.49.

3.2. Effect of Substrate and Storage Condition on Fractal Formation. As suggested by earlier study [18], growth pattern of boric acid depends strongly on the type of material and the surface condition of substrate. We have monitored growth at two different substrates in two different conditions. The substrates were borosilicate glass and poly propylene at two different humidity levels. The main observations were as follows.

(i) In glass Petri dish, samples stuck to it while in polypropylene they can be easily taken out as shown in optical photograph given in Figure 3(a).

(ii) Besides, branches become sharper in glass Petri dish instead of polypropylene. This sharpness was further controlled by atmospheric humidity.

(iii) In low humidity atmosphere (20% RH), the growth is quite thick and multilayer; hence branches are not very clear, whereas in high humid atmosphere (70% RH) the branches are quite sharp and well defined, with reduced multilayer.

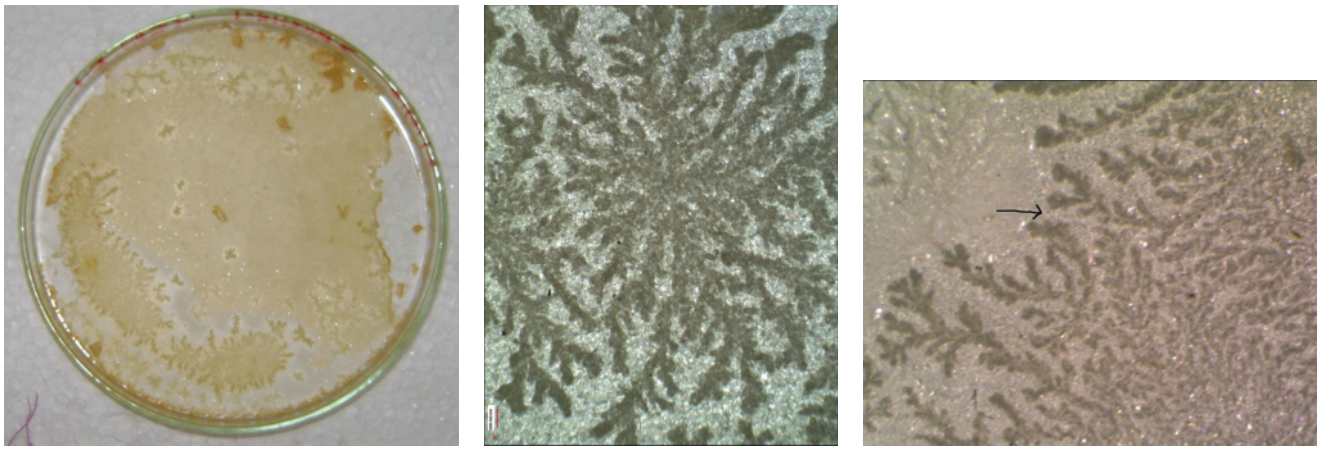
(iv) The samples kept in 20% RH were becoming orange in colour, while samples kept in 70% RH were colourless as depicted in Figures 3(b) and 3(c).

Further, the effect of humidity and substrate on fractal dimension is summarized in Table 1.

Effect of Humidity on Fractal Dimension. In low humidity atmosphere (20% RH), the growth is quite thick and multilayer, resulting in greater fractal dimension, whereas in high humid atmosphere (70% RH) the branches are quite sharp and well defined, with reduced multilayer resulting in lower fractal dimension.

Effect of Substrate on Fractal Dimension. Sharp branches are more pronounced in glass Petri dish instead of polypropylene even at a low humidity level some thick multilayer branches can be seen in polypropylene dish; therefore fractal dimension in polypropylene substrate is greater.

Sha et al. [18], while discussing the bifurcation growth of boric acid from its water solution, have discussed that boric acid molecules have an affinity towards borate glass. This affinity of boric acid towards borate glass substrate seems to be the reason why samples strongly stuck on borate glass and cannot be taken out. In the same paper, they also discussed that on PVC or Vaseline coated glass no structural growth can be seen. In present system growth is seen in both the cases, that is, in borosilicate glass and Polypropylene Petri dish.



(a) (b) (c)

Figure 1: (a) Optical photograph of the fractal, (b) close view of the ramified structure, and (c) fractal pattern where tips are not touching each other.

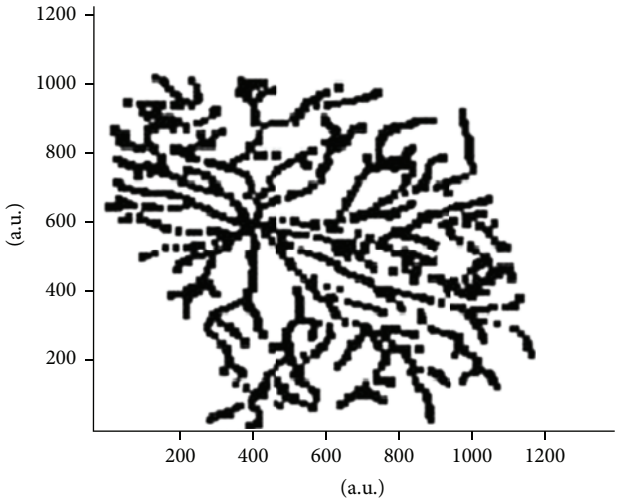


Figure 2: Extracted image of the real pattern.

Table 1: Fractal dimension of sample in different substrates a different humidity.

S. no.	Humidity	Substrate	Fractal dimension
1	20%	Glass	1.82
2	20%	Polypropylene	1.89
3	70%	Glass	1.44
4	70%	Polypropylene	1.49

Here it seems that starch matrix is playing an important role in fractal growth phenomenon. Though a very clear explanation of nucleation in the present study is not found, it is known that any kind of temperature or concentration fluctuation [15, 18] can cause nucleation. In present case, sample was prepared in methanol medium and left to dry in atmosphere. The excessive methanol will evaporate with time. Probably evaporating molecule is disturbing the local concentration, and when suitable numbers of particle are around, then they result in nucleation site. Besides, it is also observed that whenever the Petri dish surface is not smooth, density of fractal growth was higher especially in case of glass Petri dish; this was very prominent.

The difference in colour found was attributed to the presence of glutaraldehyde. As it is a known fact in aqueous solution of glutaraldehyde, GA is present in the monomer form, while nonaqueous form contains polymeric chain [26, 27]. GA is known to be in colourless to pale straw coloured form. It is supposed that the polymeric form contains large number of monomer units so the colour darkens and becomes orange in colour. As the sample was kept in 70% RH which means abundance of water, so the GA was present in monomer form; while the sample kept in 20% RH, was deprived of water, so the GA was in the polymeric form. Hence the difference in colour occurs.

3.3. Morphological Study (SEM). Figure 4 shows SEM micrograph at 200 magnifications. The micrographs show granules with some sticky structure on that. The granule can be perceptibly assigned to potato starch morphology as we have discussed in our earlier studies [28, 29]. The granule size varies from 62 μm to 35 μm. As seen in the optical micrograph the fractal structures are embossed on the starch film. For gold coating (required for SEM measurement) material is dried up to 10^{-6} Torr; hence, it seems that layer of embossed structures was detached from the film. Thus only an impression is left on the starch structure indicating presence of boric acid which will further be confirmed using other techniques in the paper. The size of crystallites in embossed structure is estimated by magnifying the image 1600% and is found to vary from ~8 μm to 22 μm. The estimation has a chance of being underrestimated and not exact as it was quite difficult to separate out the embossed structure size from the grains size of potato starch.

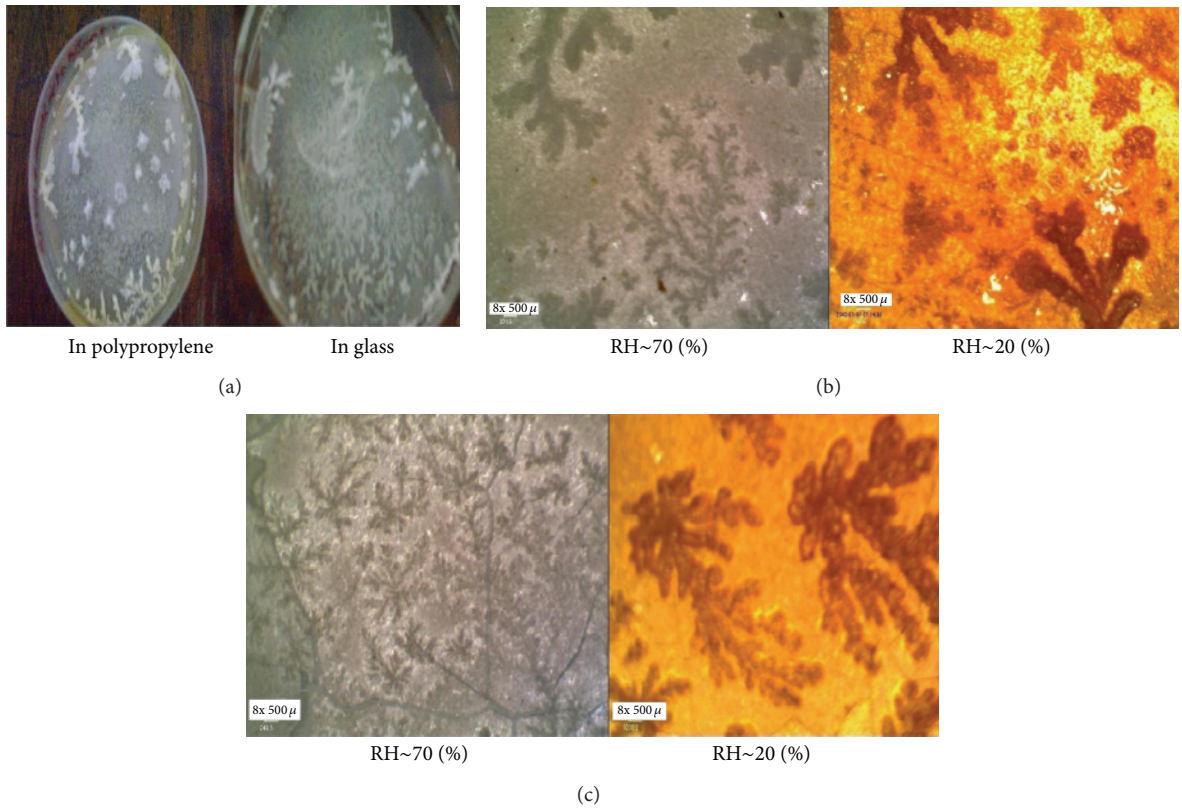


FIGURE 3: (a) Sample in polypropylene and glass Petri dishes. (b) Sample kept in different humidity levels in polypropylene Petri dish. (c) Sample kept in different humidity levels in glass Petri dish.

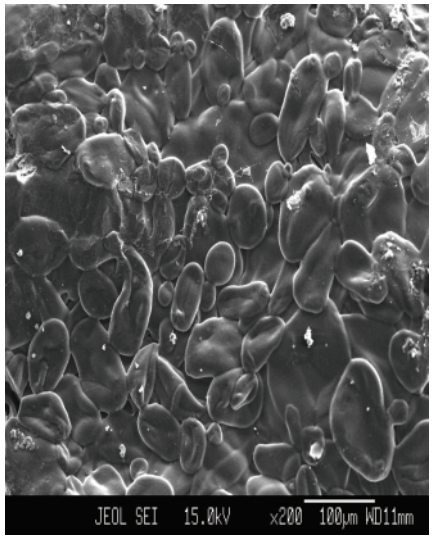


FIGURE 4: SEM micrograph of the complexed system.

3.4. Possible Chemical Structure. It is a known fact that hydrogen borate splits into tetrahydroxyborate and hydrogen ion on addition of water as given by the following reaction:

$$H_3BO_3 + H_2O \longrightarrow B(OH)_4^- + H^+ \quad (3)$$

Structure possibilities of boric acid with phenol groups are discussed in literature which shows that while interacting, with materials having multiple hydroxyl groups, boric acid uses two hydroxyl groups and then a water molecule is liberated. Applying the same concept the possible structure for starch and boric acid are presented. In Figure 5(a), structure of cross-linked host polymer with GA is given [30]. There is possibility for tetrahydroxyborate anion to make bond with its electronegative oxygen at any –OH site by removing water. One such structure is shown in Figure 5(b). The structure is supported by FTIR where the removal of –OH from the structure is clear.

3.5. FTIR Analysis. For structural changes vibrational spectroscopy is one of the major tools and is widely used. By comparing the prepared materials peak with that of original, one may get a picture of the elements and their bond vibration through FTIR analysis. In present study, system has been analyzed in transmission mode FTIR. Figure 6(a) shows the transmitted peaks of pure as well as complexed materials. Inferences drawn are listed as follows.

(i) Most of the H_3BO_3 peaks are present in the complexed system

(ii) The peaks at 641 cm^{-1} and 811 cm^{-1} are shifted to 648 cm^{-1} and 803 cm^{-1} which indicate the interaction of matrix and boric acid.

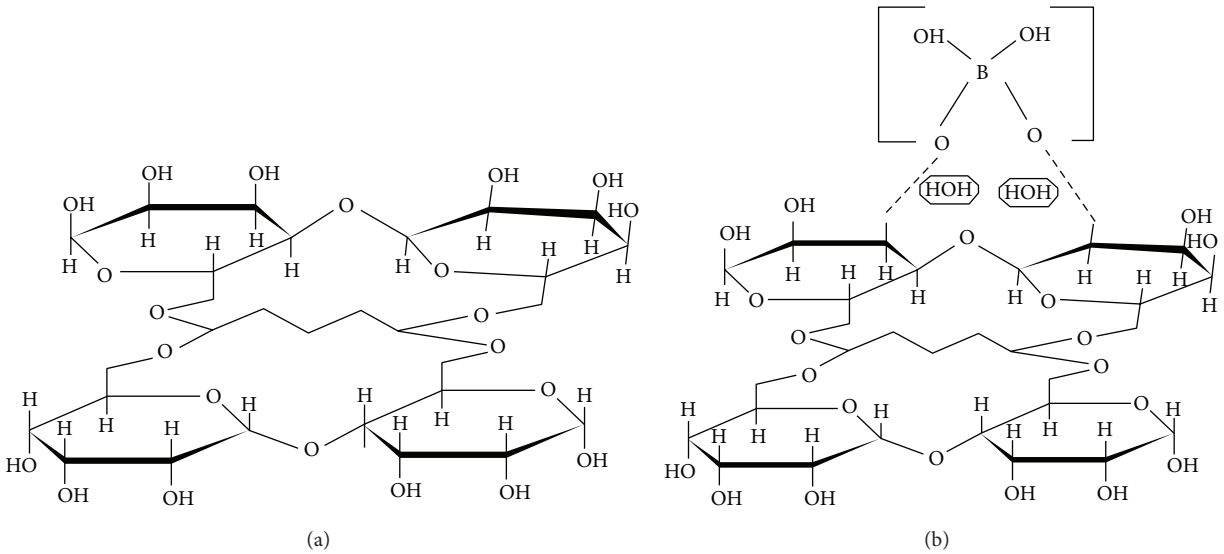


FIGURE 5: Structure of potato starch with GA (a) before and (b) after complexation.

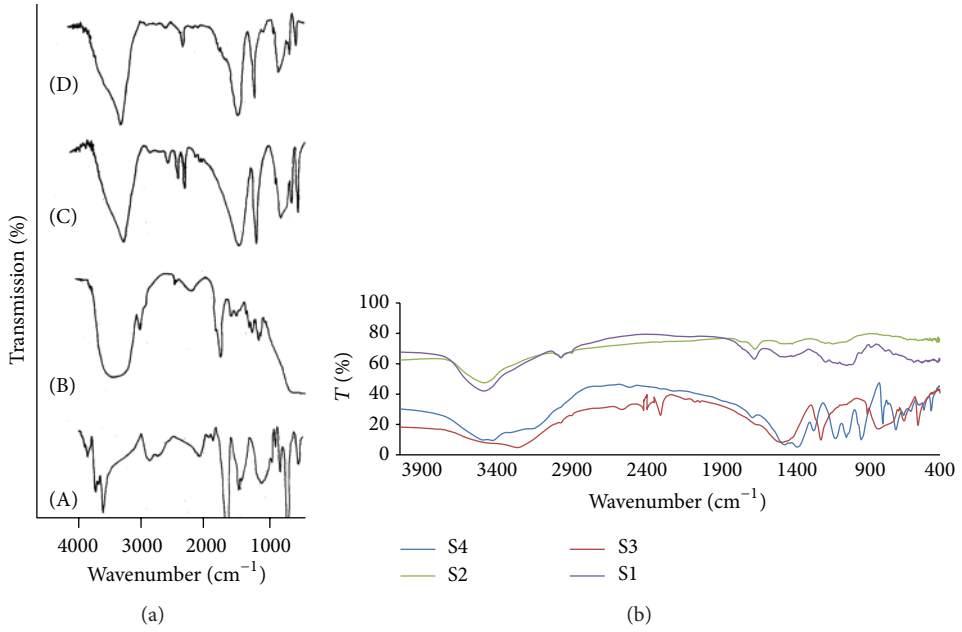


FIGURE 6: (a) FTIR of (A) potato starch, (B) GA, (C) boric acid, and (D) complex material. (b) FTIR of S1: sample kept in 20% RH, that is, relative humidity (without growth region) S2: sample kept in 70% RH (without growth region) S3: Sample kept in 70% RH (growth region only), S4: Sample kept in 20% RH (growth region only).

(iii) The 1026 cm^{-1} peak in complexed system is due to the formation of structure forming B_4-O groups.

(iv) 1194, 1462 cm^{-1} in the pure hydrogen borate is present almost at the same wave number showing vibration of atoms in –O-B< bond in orthoboric acid.

(v) The peak at 1623 cm^{-1} is solely due to presence of aldehyde group.

(vi) The intermolecular hydrogen bonding is present in hydrogen borate at 3214 cm^{-1} and in the complex at 3216 cm^{-1}.

It must be noted that in the pure starch there are a lot of hydrogen bonding peaks indicating the presence of water, but in the complexed system only one such peak at 3216 cm^{-1} could be found. This is an obvious change since addition of both GA and borate is decreasing the concentration of –OH bonds. Beside this both are occupying the space in matrix

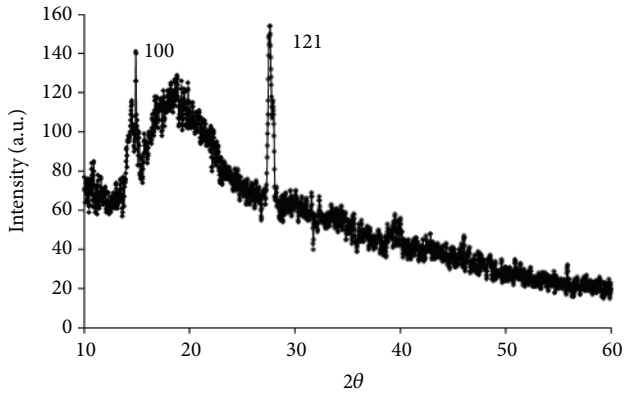


Figure 7: XRD pattern of complexed system.

hence will also reduce the amount of water absorbed in the system.

It has been tried to analyse the spectroscopic changes in the data of the following:

(i) sample kept in 20% RH, that is, relative humidity (without growth region): S1

(ii) sample kept in 70% RH (without growth region): S2

(iii) sample kept in 70% RH (growth region only): S3

(iv) sample kept in 20% RH (growth region only): S4.

Figure 6(b) shows the IR spectra of above four materials. The data taken from the matrix shows, where there is no fractals growth peaks of boric acid are missing and the portion taken from fractal growth area are dominated by boric acid peaks confirming that ramified patterns are made up of boric acid.

As stated earlier that the fractals are grown in two different atmospheres one in the ambient (70% RH) and other in the low humidity (20% RH), we found that surprisingly fractals from 20% RH or low humidity atmosphere have some peaks related to starch also, whereas the sample kept at ambient atmosphere or 70% RH have very nominal representatives of starch peaks. It is supposed to be due to the possibility of easy movement of boric acid ion assisted by presence of high water content, but when the sample kept at 20% RH, the movement of boric acid ions, is correlated with starch and salt ions are comparatively more bound with starch matrix.

3.6. XRD Analysis. The XRD pattern of complexed material is shown in Figure 7. The data is in agreement with JCPDS and clears the presence of hydrogen borate. The peaks with their corresponding planes are given in Figure 7. The two major intense peaks present at the position ($^\circ 2\theta$) 14.8997 and 27.5618 corresponds to the plane (100) and (121) of hydrogen borate. From the XRD pattern it is evident that the presence of biopolymer as a host matrix is giving the amorphous nature to the complexed system.

4. Conclusion

Phenomenon of large size (of cm dimension) fractal growth, without external stimuli, in the potato starch system has been studied. Growth pattern was found to be of DLA type with fractal dimension of 1.49. Fractals dimension depends on humidity and substrate. At high humidity and in glass substrate its value is low. System is of amorphous nature, but the presence of H_3BO_3 is giving some crystalline peak in XRD pattern. Fractal structures were found to be embossed on granule structure of potato starch. Further, the crystallite size of embossed structure estimated from SEM is found to be of the order of crystallite size estimated from XRD.

Acknowledgment

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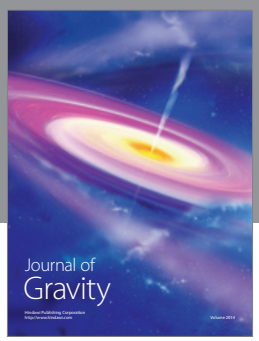

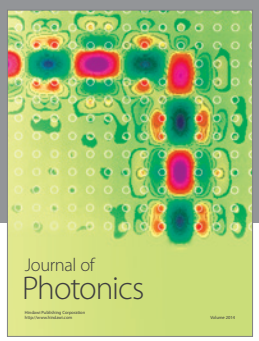

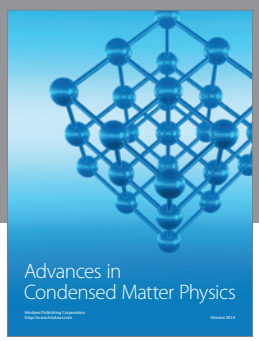

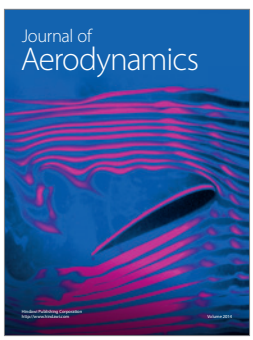

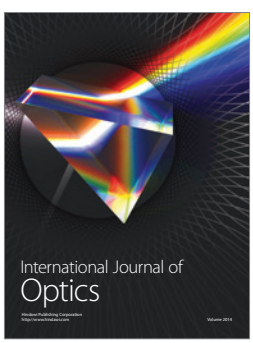

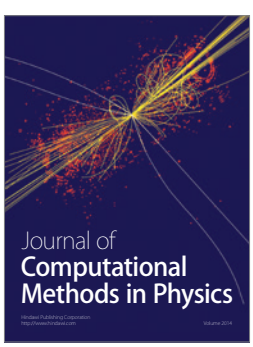

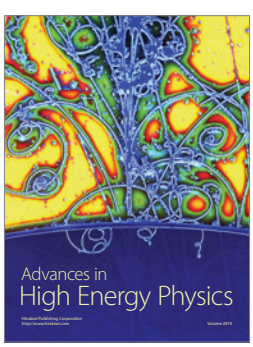

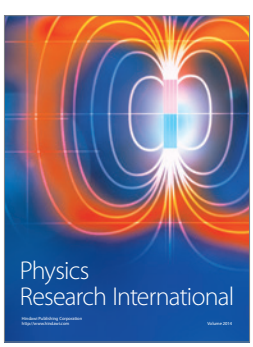

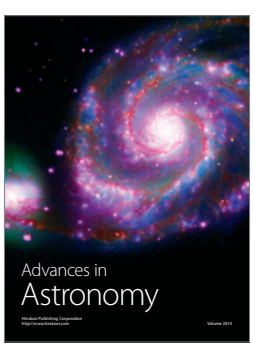

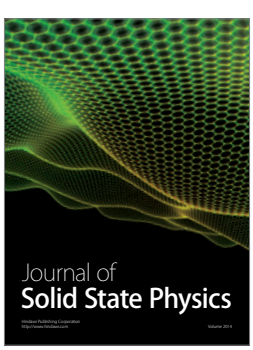

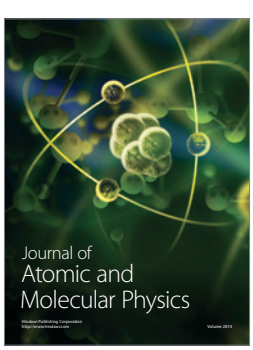

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