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RESEARCH ARTICLE

MORPHOLOGICAL STUDY OF GRAFT COPOLYMERS OF MAIZE STARCH WITH ACRYLAMIDE AND METHACRYLAMIDE

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ABSTRACT

The graft copolymers of granular maize starch with two vinyl monomers namely- acrylamide and methacrylamide were synthesized using ceric ammonium nitrate. Gravimetric estimation was used to calculate percent grafting. While acid hydrolysis and infra-red spectroscopy was used to confirm the grafting. Scanning Electron Microscopy (SEM) is the right technique to study the surface morphology of starch spherulites as their size ranges between 3 and 100 µm. The study of SEM photographs of pure granular maize starch granules and starch-graft-acrylamide and starch-graft-methacrylamide was carried out at different magnification. It was observed that surface morphology of starch changes on grafting with these monomers and is easily distinguishable from that of pure starch. In case of starch-graft-acrylamide, although the granules remained almost separate from each other, their shape changed from spherical to polyhedric. The SEM photographs of starch-graft-methacrylamide, revealed that the grafted polymer formed a thin layer on the surface of starch granules and most of the granules were joined through the surface layer of grafted polymer. SEM studies can thus be used not only to confirm grafting onto starch spherulites but if method is properly standardized can be used to characterize the graft polymer.

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INTRODUCTION

Starch is a renewable resource, cost effective biopolymer. Chemically modified starches with improved properties are gaining increasing importance in industry not only because they are low cost but mainly because the polysaccharide portion of the product is bio-degradable causing the finished product to loose its integrity and be reduced to particles small enough to be of minimal damage to the environment. Chemical modification of starch is generally effected by grafting vinyl monomers onto it. Ceric ion initiation is one of the preferred method for the synthesis of starch graft copolymers due to its simple mechanism of single electron transfer, low activation energy and formation of free radicals directly onto starch. Scanning electron microscopy became widely available in late 1960's. It is quite sophisticated instrument, relatively easy to operate and information it provides comes in the form of magnified images, which are normally easy to interpret. It provides unique information about surfaces of materials and is outstanding technique for topographic examination. Jane *et al*. (1994) carried out a systematic morphological study of 54 starches obtained from a wide variety of plant sources in terms of SEM photographs at magnification of 1500X. When Guber *et al* (1972) and Trimnell *et al* (1996) studied SEM micrographs of starch grafted with methyl acrylate, acrylic acid, acrylamide and its methacryclic analogs, they did not find any change in the shape and appearance of starch granules on grafting, however, a thick layer of synthetic polymer was observed on the surface of starch granules by Misra and Dogra (1980). In our work on starch-graft-acrylic acid, SEM photographs revealed that grafting is purely a surface phenomenon (Athawale and Lele , 1998). Fanta *et al*. (1976) used this technique to study the distribution of synthetic polymer in grafted starch granules of wheat and corn starch and noted that at higher percent grafting the granule size of corn starch, increased significantly.

While Gao *et al.* (1994) observed that the granular structure of canna starch altered drastically when methyl methacrylate was grafted onto it. Sadeghi and Behrouz, (2011) used this technique to characterize surface and cross section of hydrogel based on gelatin. Kalia *et al.* (2011) when studied the morphology of original sunn hemp fibres and grafted fibres with etyl acrylate and binary monomers, observed that original fibres were smooth and the smoothness was grossly affected on grafting. Pathania *et al.* (2012) used this technique to characterize graft copolymers of gelatinised potato starch, to

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find that the surface graft copolymer becomes coarse as against smooth surface of pure starch. Kaur and Sharma (2012) used SEM analysis for characterizing sago starch grafted with acrylic acid. (Athawale and Lele, 1998) and Athawale *et al* (1998) have reported the optimization of reaction conditions of granular maize starch grafted with acrylamide (AM) and methacrylamide (MAM) respectively in earlier articles. However, it is equally important to study the change in morphology of starch granules on grafting these vinyl monomers onto it by using scanning electron microscopy (SEM) technique. The present communication describes the surface morphological study of pure granular maize starch and of the newly formed graft copolymers namely starch-graft-AM and starch-graft-MAM using SEM technique.

MATERIALS AND METHODS

Materials

Maize starch (Food grade), supplied by Rajaram and Bros., Mumbai, India was first dried at 110^0C and then was stored over anhydrous $CaCl_2$. Acrylamide (AM) (J. T. Baker Chemical Co., NJ, USA), was purified by recrystallization with acetone and then stored over $CaCl_2$ in vacuum desiccator. Methacrylamide (MAM) (LR grade, Sisco-chem Industries, Mumbai, India) was purified by recrystallization with methanol and then stored over $CaCl_2$ in vacuum desiccator. Ceric ammonium nitrate (CAN) (J. T. Baker Chemical Co., NJ, USA), was dried in over at 110^0C and then stored over $CaCl_2$ in vacuum desiccator. It was used as 1.0 mol/L solution prepared in molar nitric acid (AR grade, s. d. Fine Chemicals, India).

Graft copolymerization

The reaction was carried out by taking the mixture of 2 g of dried starch with 70 mL of water and stirring magnetically under nitrogen atmosphere to make a uniform slurry. It was the treated with predetermined quantity of CAN for 10 min to facilitate free radical formation on it, It was followed by addition of monomer and then the total volume was made to 100 mL with distilled water. After certain time, the reaction mixture was immediately filtered through preweighed Whatman filter paper no. 41. The residue was made free of homopolymer by repeatedly washing with warm water, till the extract gave no precipitation with methanol. After extraction of homopolymer the residue was dried in air-oven at 110^0C. The details of the reaction conditions at which the samples used in present study, were synthesized are listed in Table 1.

Grafting parameters

The grafting parameters namely the percentage grafting efficiency (%GE) and percentage grafting (%G) were based on gravimetric estimation and were calculated as follows:

$\%GE = 100 (W_2 – W_1) /W_3$
$\%G = 100 (W_2 – W_1) /W_1$
Where W_1 W_2 and W_3 are the weights of pure starch, graft copolymer and monomer charged respectively.

Scanning electron microscopic analysis

The SEM analysis was carried out using Scanning Electron Microscope (SEM) of Cameca (France) model SU 30. The specimens in the form of films were mounted on the specimen stabs and coated with thin film of gold by the ion sputtering method. The micrographs were taken at magnification of 700, 1000 and 1500 using 20 KV accelerating voltage.

RESULTS AND DISCUSSION

All starches occur in nature as minute granules (3-100 μm), each with its inherent characteristics, size and shape. The source of a starch can be identified from its microscopic appearance. SEM is the unique technique used for direct observation of microstructure of spherulites. of size ranging from 0.1-10 μm. Size of maize starch granules ranges between 3-26 μm and are round to polygonal in shape. In present study, the electron micrographs of pure starch (Fig.1) reveal its granular structure, whereas, graft copolymers (Fig.2 and 3) showed variation in morphology.

SEM micrographs for pure starch displayed better resolution only at the magnification of 1000 and 1500. The granules of pure starch looked almost spherical or somewhat polygonal in shape and were separated from each other (Fig.1 A and B). The graft copolymers of starch and AM showed more of the irregularity in shapes of granules with a number of faces (polyhedric) and relatively sharp edges. Although most of the granules were still separate, few granules were connected to each other through the outer coating of the grafted PAM chains (Fig.2 A, B and C). Further it can be seen that the size of the granules has considerably increased in comparison to the pure starch granules. The %G in case of AM is much higher of the order 51.80%. Hence increase in size of the granules can be attributed to the thick layer formation of grafted chains of polyacrylamide (PAM) on the surface of the granules.

Table 1. Graft copolymerization data and grafting parameters for starch graft copolymers

Polymer	[Monomer] mol. L^{-1}	[CAN]/ mol. L^{-1}	Temperature /^{0}C	Time / min	% GE	% G
S-g-AM	1.125	0.010	30	180	12.95	51.80
S-g-MAM	0.705	0.004	30	180	10.40	31.20

Confirmation of grafting

The confirmation of grafting was done based on acid hydrolysis of grafted samples followed by IR spectral analysis of pure maize starch and graft copolymer. The details are mentioned in our earlier studies.

In case of grafting of MAM, the electron micrographs disclosed that the grafted starch granules are no longer separate from each other. Most of the granules had joined to each other to form ring structures. Obviously the material connecting the granules must be the surface grafted polymer chains of polymethacrylamide (PMAM).

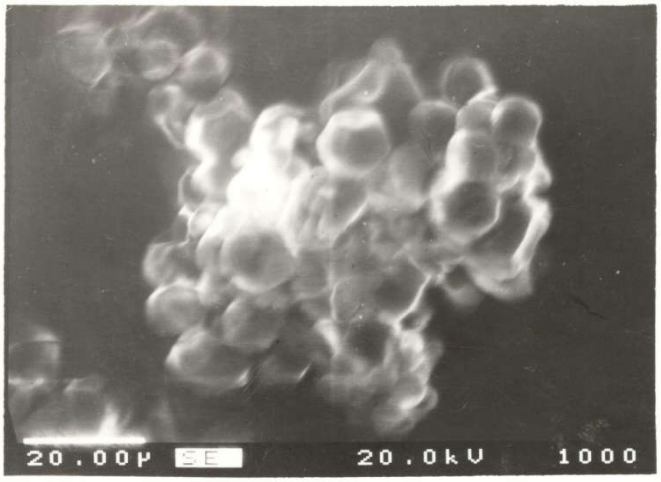

Figure 1(A). SEM of Pure Granular Maize starch at Magnification 1000

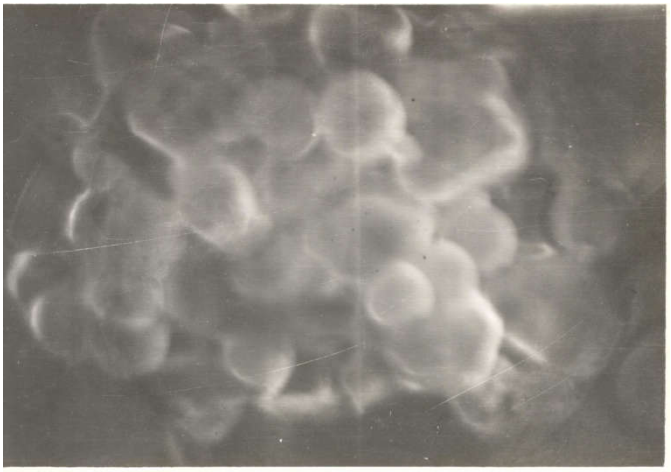

Figure 1(B). SEM of Pure Granular Maize starch at Magnification 1500

Hence it can be said that MAM is grafted mostly on the surface of starch granules and does not penetrate into the granules and that the grafted chains can extend from one granule to other thus combining these granules.

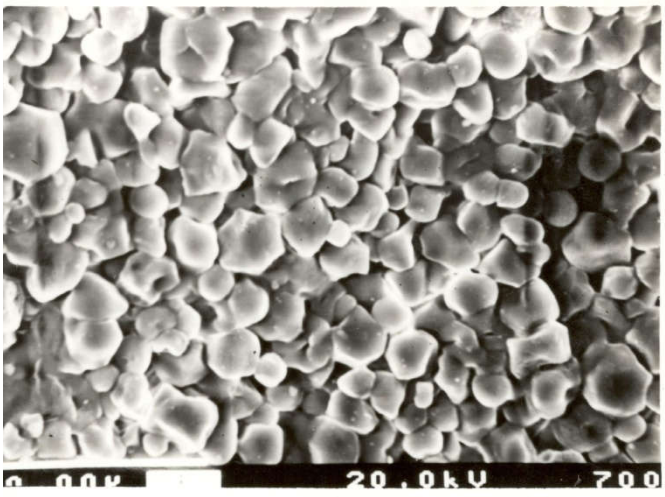

Figure 2(A). SEM of Starch-graft-AM at Magnification 700

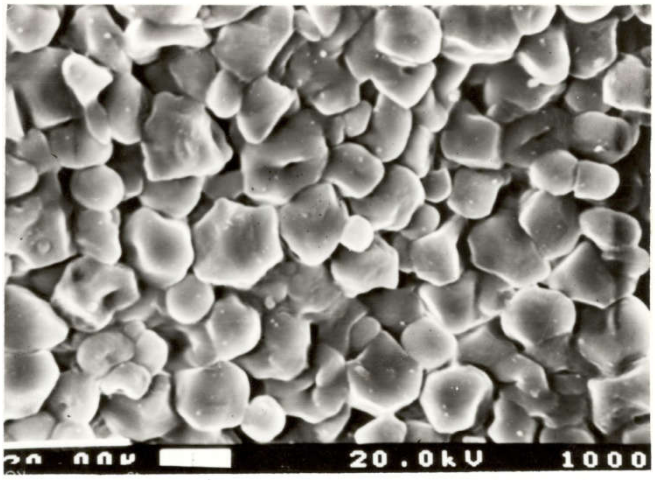

Figure 2(B). SEM of Starch-graft-AM at Magnification 1000

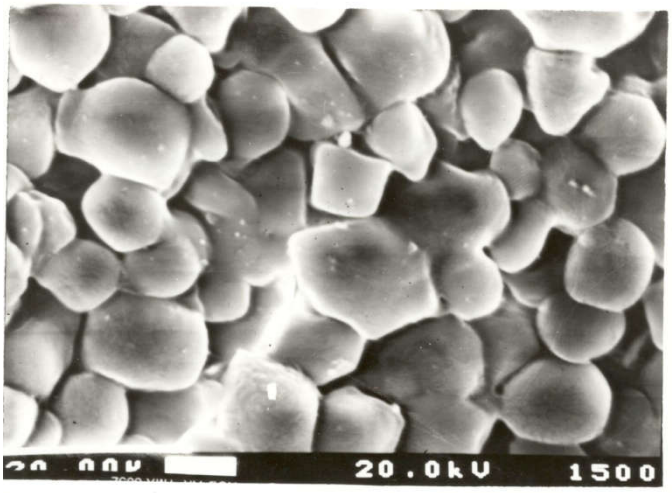

Figure 2(C). SEM of Starch-graft-AM at Magnification 1500

The %G in case of starch-graft-MAM is quite low of the order 31.80% hence it can form only a thin layer as it is also used up in joining the granules which is evident from the unaltered shape and size of the grafted granules joined to each other (Fig. 3 A, B and C).

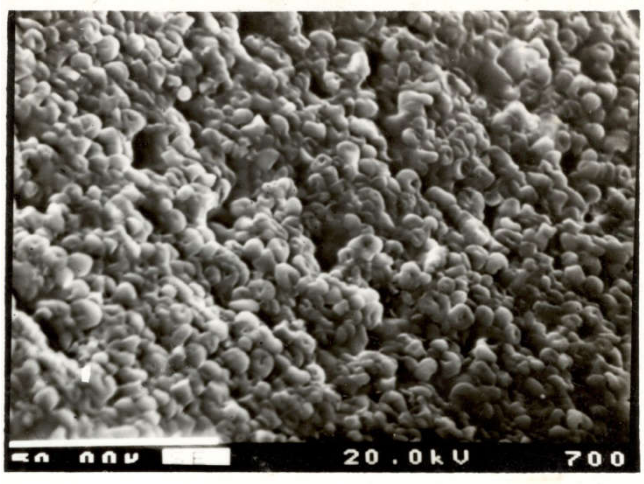

Figure 3(A). SEM of Starch-graft-MAM at Magnification 700

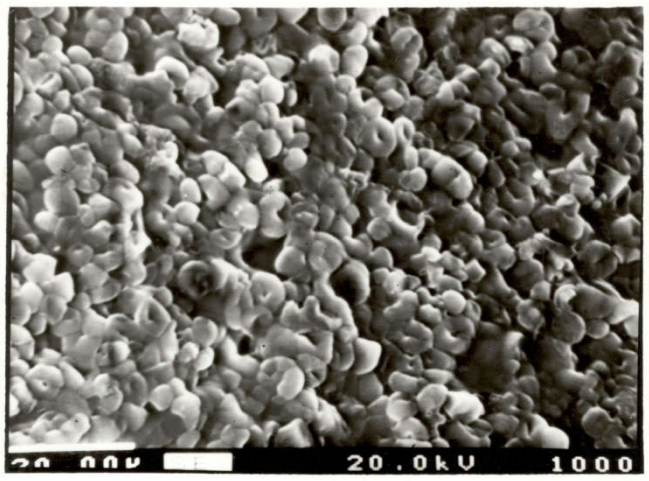

Figure 3(B). SEM of Starch-graft-MAM at Magnification 1000

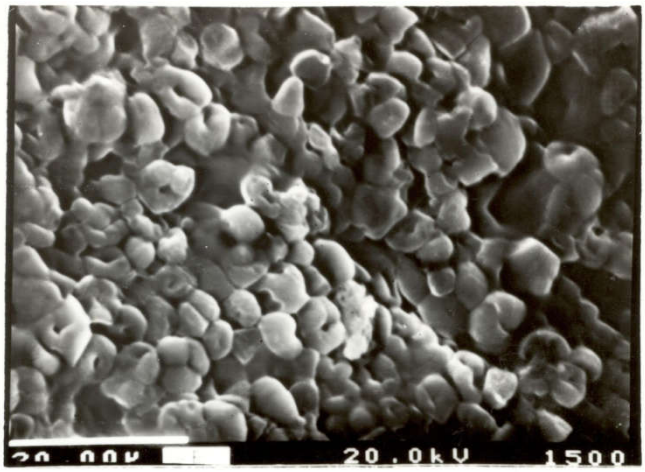

Figure 3(C). SEM of Starch-graft-MAM at Magnification 1500

Conclusion

In earlier research articles on graft copolymerization on starch, the three methods namely gravimetric estimation, acid hydrolysis and Infra-Red Spectroscopy have been used to confirm the formation of graft copolymer. However, Scanning electron micrographs give the visual and hence direct evidence of the grafting of vinyl monomers onto starch. These micrographs are useful in studying changes in morphology of spherulites such as pure starch on grafting vinyl monomers onto it. Although methacrylamide is the homologue of acrylamide, it shows different pattern of grafting onto starch. This is possible to study due to SEM technique. Therefore, not only the SEM technique can be used as an evidence of formation of graft copolymer but after proper standardization, these micrographs can be used even to characterize different starch graft copolymers.

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