Green Technology Based Nanostarch Films: Water Vapour, Thermal Properties and Micro structural Properties Detection

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Abstract: A process tried to be developed to prepare starch nanocrystals other than conventional method of acid hydrolysis. Further comparative structural studies in between the films incorporated with acid hydrolysed starch nanocrystals and green technology based nanocrystals, are carried out by Scanning electron microscopy. It is observed that a lower content of starch nanocrystals showed smoother than high starch nanocrystals in a rice starch film matrix in case of acid treated starch nanocrystals. A uniform smoothness is observed in case of green technology based starch crystals both at high and low concentration. With the increase in content of rice starch Nanocrystals (from 5% to 20%) prepared from green technology results in decrease in water vapour permeability and no nanopores or nanocraters are observed in nanostarch films prepared by green technology compared to acid hydrolysis based nanostarch films.

Key words: rice-starch, nanocrystals, green technology, water vapour permeability, soluble matter

I.INTRODUCTION

Environmental pollution leads to usage of biodegradable plastics. Such biodegradable plastics can be made from starch which is cost effective. Since starch based films are of very poor moisture barrier properties protein blends are used so as to overcome such issues, reports are observed (Jagannath et al 2003). Starch films made from corn (Choudhury et al 2012), cassava(Zhong et al 2008), wheat, potato (G.Hu. etal 2009), pea, sago (Hanisa etal 2011) and rice (Thawien Wittaya 2009) so far reported. The film properties of starch based films are now being improved by using certain improved technology, either by modifying starch materials or by incorporating nanocrystals of starch in control films. The conventional method for preparing nanocrystals is acid hydrolysis (Coussy et al 2009). Though from previous literature it is observed that starch nanocrystals incorporated films do have better mechanical properties though some issues are raised like nanopores are observed from micro structural studies of the films (Piyada etal 2012) which can create void space leading to poor quality. Hence the objective of the present work is to produce rice starch nanocomposites using starch nanocrystals prepared from green technology instead of using conventional acid treatment. The effects of starch nanocrystals on rice films are assessed on the basis of mechanical, thermal and structural properties.

II.MATERIALS

Native rice starch, polyethelene glycol (400), glycerol, ethanol are analytical grade provided by E-Merck Pvt.Ltd. Mumbai.

III.METHODS

A. Preparation of starch nanocrystals

Green technology developed for Nanostarch crystals preparation comprises mainly two ways; a) Starch added to polar solvents like glycerol, Polyethylene glycol 400 and gelatinized at 70°C for a certain period of time till gelatinization occurs. Further such gelatinized starch is treated with ethanol and nano crystals of starch are obtained by micropipetting. b) Starch first homogenized with Glycerol and later ethanol washed by centrifugation at 6000rpm for 15minutes and the residue is collected. The resulting nanocrystals are generally observed in the form of an aggregates having an average size of 356nm as measured by Differential Light scattering technique by Laser particle size analyzer. Another technique using conventional method of acid hydrolysis is carried out to prepare starch nanocrystals (Piyada etal 2012)

B. Film Preparation

A starch solution with a concentration of 3% (w/v) was prepared by dispersing rice starch in distilled water and heating the mixtures and stirring until it gelatinized (85°C for 5 min). It was then cooled to 45±2°C. Subsequently, the starch nanocrystals dispersion was added at 5, 10, 15, 20, 25, and 30% of starch and stirred for 2 min. The mixtures were cast onto flat, leveled, non-glass slides. Once set, the slides were held at 90°C for 15 minutes in hot air oven undisturbed, and then cooled to an ambient temperature before peeling the films off the slides. The film samples were stored in plastic bags and held in desiccators at 60% RH for further testing. All treatments were made in triplicate.

C. Film Testing

The morphology of the rice starch films was observed with a Scanning Electron Microscope (SEM, HITACHI SEM (S-3400N, India) (Tanima Bhattacharya etal 2013). The size of the rice starch and starch nanocrystals was observed using a differential light scattering technique. (LS-230, Coulter, U.S.A.) TGA and DSC also carried out to check the thermo stability of the films. Water vapor permeability (ASTM method) (Tanima Bhattacharya etal 2013). Film solubility
IV. RESULT AND DISCUSSION:
The morphology of the Green technology based starch nanoparticles examined by Scanning electron microscopy (SEM) as indicated in fig1.

**Fig 1:** Morphology of green technology based starch nanocrystals

From the Fig1. it is noted that the crystals are pointed at both the ends as cited in literature of Angellier et al 2009 (Transmission electron microscopy images gives the dimension of 50-100nm), here the particle size ranges from 300-400nm. The crystals noted are pointed at both the ends as cited in Piyada et al 2012, 50-100nm gives aggregation of 3.4micrometer thus 300-400nm will give aggregate of 5 micrometer (the relationship is derived during the study). Though the acid hydrolysed starch nanoparticles are of smaller dimensions, but later certain contradictory characteristics are observed in nanocoating incorporated with such crystals which may even weaken the properties of such films. Study of Morphology Nano Particles incorporated films by Scanning Electron Microscopy

**Fig 2.** This is the scanned photograph of the literature Piyada et al 2012.

This photograph reveals the nanopores or nanocraters that are formed on incorporating acid treated nanocrystals in the rice starch films.

A comparative study can be done in between the SEM images of the acid treated crystals incorporated films, and green technology based films from fig 2 and fig 3. In fig 2, nanopores are observed (Piyada et al 2012, when acid treated nanostarch are incorporated in the rice films at 20%) but no such observations are cited in fig 3. green technology based films. Thus one conclusion can be drawn that these; porosities are due to acid crystals as acid used is corrosive in nature it has a negative impact on the film properties than the latter.

**TGA/DSC Study of the nanoparticles incorporated starch starch films:**

**Fig 4.a.** Rice starch films incorporated with 15% acid treated nanocrystals starts degradation beyond 40°C (with higher water loss observed)

**Fig 4b.** Rice starch films incorporated with 20% starts degradation beyond 40°C with a unique water loss
Fig 4c. Rice starch films incorporated with 15% green technology based starch nanocrystals starts degradation beyond 50°C

Fig 4d. Similarly, 20% green technology based nanocrystals when incorporated in rice starch films also starts degradation beyond 50°C (no such difference with that of 15% nanocrystals incorporated films)

From Fig 4a. and 4b. it is observed that nanostarch crystals (prepared by acid hydrolysis) when incorporated in control rice starch films, shows degradation at 40°C. whereas the rice starch films incorporated with green technology based nanocrystals start degrading only beyond 50°C. It is observed that the initial weight loss at 30°C is due to evaporation of water. The weight loss in the second phase that is 40-100°C is due to complex process including dehydration of the saccharide rings and depolymerization (Mathew and Duffresne 2002). From Fig 4c. and 4d., TGA curves show that the rice starch films incorporated with green technology based nanocrystals shows better thermostability than the acid treated nanocrystals. The green technology based nan crystals incorporated films are stable up to 50°C with a maximum rate of decomposition beyond 55°C. These results indicate an improvement in the thermal stability of the films incorporated with starch nanocrystals. This is in agreement with Wang et al. (2010), for composites with starch nanocrystals and incorporating starch nanocrystals and cellulose whiskers in a waterborne polyurethane (WPU) matrix. The films containing polysaccharide nanocrystals, especially the ternary system, exhibited higher thermal resistance than pure WPU. It is worth noting that the addition of nanofillers displayed a more distinct effect of improving the thermal resistance of the hard segment. However, the rate of the thermal decomposition of the soft segment was even faster than that of pure WPU. This could be explained by the strong hydrogen bonding interactions that existed between the nanofillers and the hard segments, especially in the ternary system. These interactions induced the microphase separation between the hard and soft segments. This led to the acceleration of the decomposition of the soft segments. However, the incorporation of starch nanocrystals and cellulose whiskers also exhibited a much better reinforcing effect than starch nanocrystals reinforcement in WPU. This was because hydrogen bonding networks of polysaccharide nanocrystals and whiskers formed in the nanocomposite films. This caused the synergistic reinforcement of the WPU networks. Similarly, Kaushik et al. (2010) found that increasing the cellulose nanofibril content led to increase in the char yield of composites films. This is due to cellulose-based composites having lower water content at equilibrium, compared to unfilled thermoplastic starch. As cellulose is crystalline, its crystallinity decreased the polar character of starch. Thus the addition of cellulose into a starchy matrix decreases the global water content with a resultant increase in the cellulose nanofibril content. Typically, the thermal properties are improved and the char yield of composites films increased with the addition of fillers (Wang et al., 2010; Huang et al., 2004;). Film Solubility nanoparticles incorporated rice starch films:

<table>
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<th>Weight (g)</th>
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<th>Weight loss</th>
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<tr>
<td>40</td>
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Fig 5a. Graphical representation of Film solubility versus concentration of acid treated starch nanocrystals

Fig 5b. Graphical representation of Film solubility versus concentration of green technology based starch nanocrystals.

From Fig 5a. and 5b., it is observed that film solubility decreases with incorporation of either acid treated or green technology based nanocrystals at higher concentrations. Though there are reports on protein films (Saremmezadetal 2011) but no such reports on nanostarch films are observed in case of film solubility. Though we know that starch
materials are highly hygroscopic, but on addition of nanocrystals, their hydrophilicity is reduced. In case of packaging applications or laminating applications, water vapour invasion rate should be less(Gontard et al 1992). Relationship of water invasion and increase in nanofillers content is also highlighted by (Sinha and Okamoto etal 2003). Even reports show an increase in nanoSiO2 filler content will decrease the water vapour invasion(Mathew and Dufresne 2002), which indicates the decrease in mobility of starch particles.

Conclusion:
Further studies on mechanical and antimicrobial properties are need to be done so as to assess that this type of green technology based nanocrystals of starch incorporated films can also serve as better bioplastics and replace synthetic polymers.

Reference: