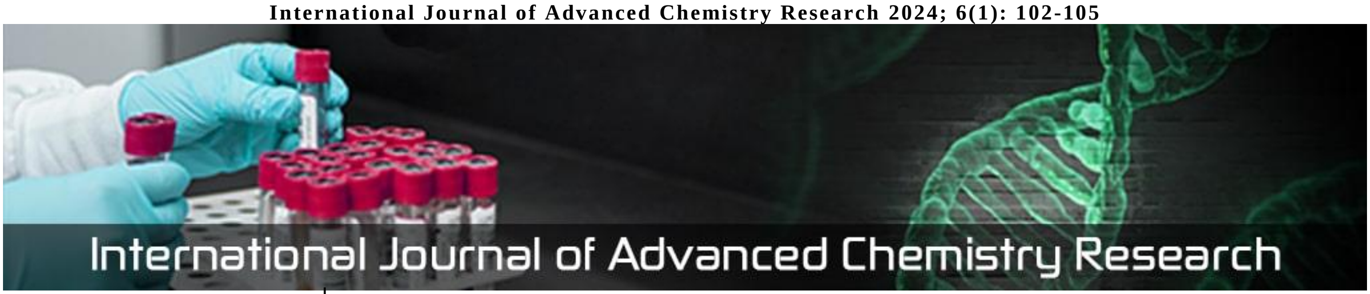

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Water sorption behaviour of PVA-starch binary polymer blends

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Abstract
Polymeric materials are extensively utilized worldwide today. However, their recalcitrant nature and subsequent accumulation in the environment have led to various problems. There is a strong demand for the replacement of non-biodegradable polymers with biodegradable ones in specific sectors such as food packaging and medical devices, where recycling is not recommended. Biodegradable polymers can be categorized as natural-based materials and synthetic polymers. Polysaccharides and other essential macromolecules such as proteins belong to natural-based materials. This paper focuses on their application in food and cosmetic packaging, as well as solar energy. While each polymer presents specific properties, they also have limitations that prevent them from meeting the diverse performance requirements for packaging materials. Consequently, multilayer structures are commonly used to overcome specific disadvantages such as high cost, low barrier, and mechanical properties.
Polymers like starch and polyvinyl alcohol (PVA) can offer mechanical properties at low cost, while barrier polymers such as polyamides and ethylene vinyl alcohol can provide protection against gases, flavours, and odours within the packaging. However, the main drawback of these multilayer packages is their challenging recycling and reprocessing into new products. The exponential increase in the production and use of packages globally exacerbates the waste disposal problem. The growing interest in the environmental impact of discarded materials necessitates thermoplastic polymers that can be melted and reused as raw materials for new applications. An alternative strategy to enhance the physical properties (e.g., mechanical, thermal, degradation, barrier, etc.) of traditional polymeric systems is the incorporation of inorganic materials at the nanometre level. Additionally, chemical functionalization of such materials using active molecules with specific properties can impart new functionalities to the polymers. Other interesting prospects concern specific applications such as controlled release.
Starch, commonly extracted from wheat, rice, corn, and potato, is widely available and cost-effective, making it one of the most accepted biopolymers. Starch can be blended with other materials in proportions ranging from 30% to 80% depending on its application. Biodegradable polymers like PVA (Polyvinyl Alcohol) are commonly used as copolymers. Starch-based films are employed either as monolayers or in combination with barrier films as laminates for packaging applications. The main criterion determining the use of these biopolymers in food packaging is their potential for migration.

Keywords: Water sorption, biodegradable, polyvinyl alcohol, starch, packaging

1. Introduction
For many years, plastic like polyethylene (PE), Polypropylene (PP) and polystyrene have been widely used in food packaging industry [1] due to inappropriate disposal and environmental build up, synthetic and no biodegradable materials have caused numerous environmental issues. Because it is inexpensive and readily available, starch is a promising raw ingredient for the development of biodegradable products. Moreover, because starch is hydrophilic, its applications are limited. Consequently, a number of studies are being carried out to enhance the properties of starch-based materials. This paper provides of recent research on starch-based materials, with a particular emphasis on the creation of starch composites, starch blends with biodegradable polyester and agro-biopolymers, and nanocomposites with both organic and inorganic fillers.
Given the growing amount of food waste due to spoilage, traditional plastic packaging has versatile properties, including light-weight, resistance to destruction, low cost, and ease of manufacture and figuration [2]. Pectin-based active packaging. However, the application of plastic packaging is limited by its non-degradability, inactivity, and environmental pollution

[3]. Therefore, exploring biodegradable active materials is necessary to replace traditional plastic packaging. Several biomacromolecules, such as starch, protein isolates, pectin, and lipids, have been used to prepare bioactive edible films [4]. In particular, starch is considered an attractive film matrix because of its low cost, renewability, and abundance in nature. Potato starch is widely used for the preparation of films with favorable thickening and gelling capacities. In addition, starch films have many potential benefits associated with their excellent mechanical and barrier properties [5]. However, some studies have revealed certain limitations of pure starch-based films that can be attributed to the lack of antioxidant and antibacterial activities [6] Starch is a widely used food packaging agent due to its renewability, low cost and good processivity along with its excellent film forming properties. Starch as a packaging material has grabbed much attention both at academic as well as industrial levels. Slowly digesting starch of great significance for packaging applications [7]. The functional role of starch in food products is enormous which include its use as an adhesive for binding, film forming, gelling, glazing, moisture retaining, stabilizing, and thickening material [8]. Even though starch is widely used in the development of food packaging films, it has poor mechanical and thermal properties. To overcome this crisis, starch is blended with other polymers such as PVA and PLA, lignin etc. [9] where PVA has been reported to have excellent compatibility with starch [10]. Polyvinyl alcohol (PVA) is a hydrophilic and nontoxic polymer having excellent film forming, emulsifying and adhesive properties along with higher tensile strength and flexibility [11]. But, the major drawback of PVA is the humidity induced mechanical property changes which greatly limits its application. However, fabrication of polymers with nanomaterials has been described to improve its mechanical, barrier, thermal and biological properties. Among the nanoparticles used for such applications, Zinc oxide nanoparticles possess many desirable properties. It is nontoxic and exhibits antimicrobial, UV filtering, barrier and mechanical properties and is also listed as GRAS category by FDA. To multiplex the properties, functioning and applications of PVA, it can be blended with other materials. One of the recent trends for such applications is the use of phytochemicals like essential oil. In this work, active films based on potato starch were prepared with different content through a solution casting method. The physical, structural, antioxidant and antimicrobial activities of the composite films were investigated.

2. Materials and Methods

2.1 Materials

PVA (hot) was purchased from Merck Inc. (DP 1799 ± 50; molecular weight: 14,000; hydrolysis rate: 90%; pH: 4.5-7; density: 1.3 g/cm3). Starch containing 1.7% moisture, 0.23% protein and 0.075% fat was purchased from fine research lab Mumbai India, Soluble starch was obtained from S. Merck (India) and used without pre-treatment and distilled water and finally distilling it under vacuum.

All other chemicals and regents used were of analytical grade and bi-distilled water was used throughout the experiments.

2.2 Preparation of the nanocomposite films PVA /starch:

Starch/PVA Blends PVA is compatible with starch and blends are expected to have good film properties. If both components are biodegradable in various microbial environments, PVA and starch blends are biodegradable. The hydrophilic nature of PVA enhances compatibility with starch, making it suitable for the preparation of polymer blends. The use of PVA with starch improves the mechanical properties of the blends. Starch/polyvinyl alcohol blends are one of the most popular biodegradable plastics, and are widely used in packaging and agricultural applications. Although the processing and mechanical properties of starch/PVA blends have been investigated extensively, there is only a limited number of publications about it.

2.3 Blends preparation method

The PVA blend was prepared by PVA solution. In typical experiment 1g PVA (hot) was dissolved in 25 ml distilled water by heating 60 °C for ½ hrs on a magnetic stirrer-cum heater to get homogeneous solution. After this, the prepared solution of PVA mixture was poured onto the Petri dish and allowed to dry in oven for 24 h at 60 °C. After 24 h of drying, the fully dried membranes were peeled off from the petri plate. Transparent blend prepared was equilibrated with distilled water for 24 hrs so that the unreacted monomer, polymer and other chemicals were leached out. The fully swollen blend was cut into small discs and dried at room temperature for one day. The dried discs were semi-transparent in appearance and stored in air tight polythene bags. Native PVA Blend shown bleow figure 1.

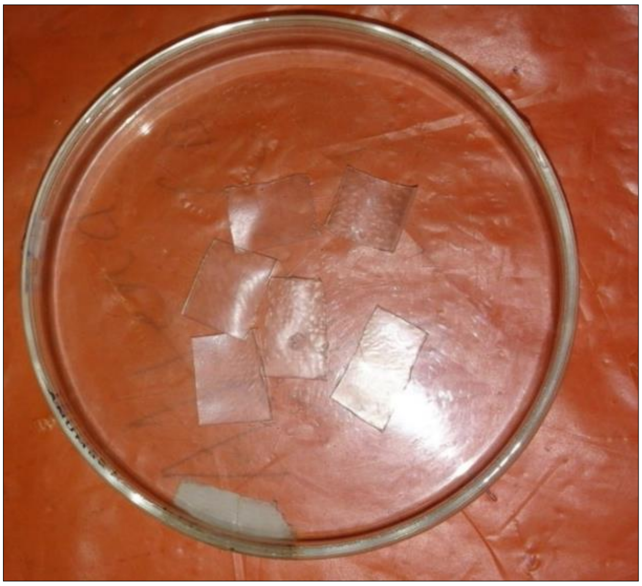

Fig 1: Physical appearance of PVA Blend (Pieces of PVA blend)

The starch/PVA blend was prepared by adding starch/PVA solution. In typical experiment 2 g PVA (hot) was dissolved in 25 ml distilled water by heating 60 °C for ½ hrs on a magnetic stirrer-cum heater to get homogeneous solution. And 0.5 g starch was dissolved in 25 ml distilled water by heating 60 °C on a magnetic stirrer-cum heater to get homogeneous solution. Starch/PVA solutions were mixed together and heated at 70 °C with constant stirring for 1/2 h. After this, the prepared solution of starch/PVA mixture was poured onto the Petri dish and allowed to dry in oven for 24 h at 60 °C. After 24 h of drying, the fully dried membranes were peeled off from the Petri plate. Transparent blend prepared was equilibrated with distilled water for 24 hrs so that the unreacted monomer, polymer and other chemicals were leached out. The fully swollen blend was cut into small discs and dried at room temperature for one day. The dried discs were semi-transparent in appearance and stored in air tight polythene bags. Figure 2. Shown starch -PVA blend.

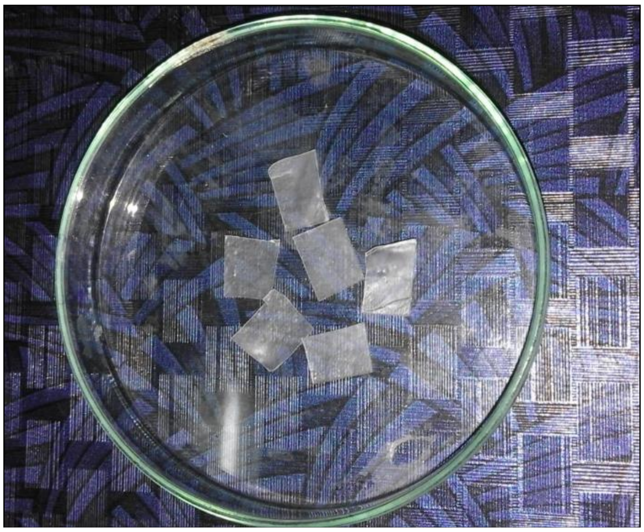

Fig 2: Shown starch -PVA blend

2.4 Characterization of nanocomposite film

Water Sorption Studies

The major drawback of starch-based films is its hydrophobicity. On the other hand, the degree of absorption of water and thus swelling of PVA-Starch based polymers is of utmost importance, if they are to be used for biological applications. Thus, water absorption at pH 1.8, pH 7.4 and pH 8.6 were done. Samples of 2:0.5 blends were weighed and placed in the different solutions. The weights of the samples were monitored at the end of the first 30 minutes, 60 minute, 90 minute, 120 minute and 180 minutes. The percentage increase in weight was tabulated and that was taken as a measure of the water absorption of the blend. Blends pieces (1 cm x 1cm) were conditioned at 50 °C for 3 h and weighed (W dry). Dried blends were immersed in distilled water at room temperature (25 °C) for 24 h. After 24h, samples were removed from the beakers containing distilled water, dried by wiping gently with blotting paper and subsequently weighed (W wet) to determine water absorbed by the films. The water absorption (Wa) is given by [13].

$$\% \, W_a = \frac{Wwet - Wdry}{Wdry} \times 100 \quad (1)$$

2.5 Effect of water sorptions in biopolymer

2.5.1 Effect of amount of starch

In present study, the effect of increasing concentration of starch on the swelling behaviours of blends has been observed by polymerizing of starch in mixture is in increasing concentration range from 2.52-2.73. The result shown Figure 3 (Table- 1) which show clearly that the equilibrium ratio of the blend increasing ratio.

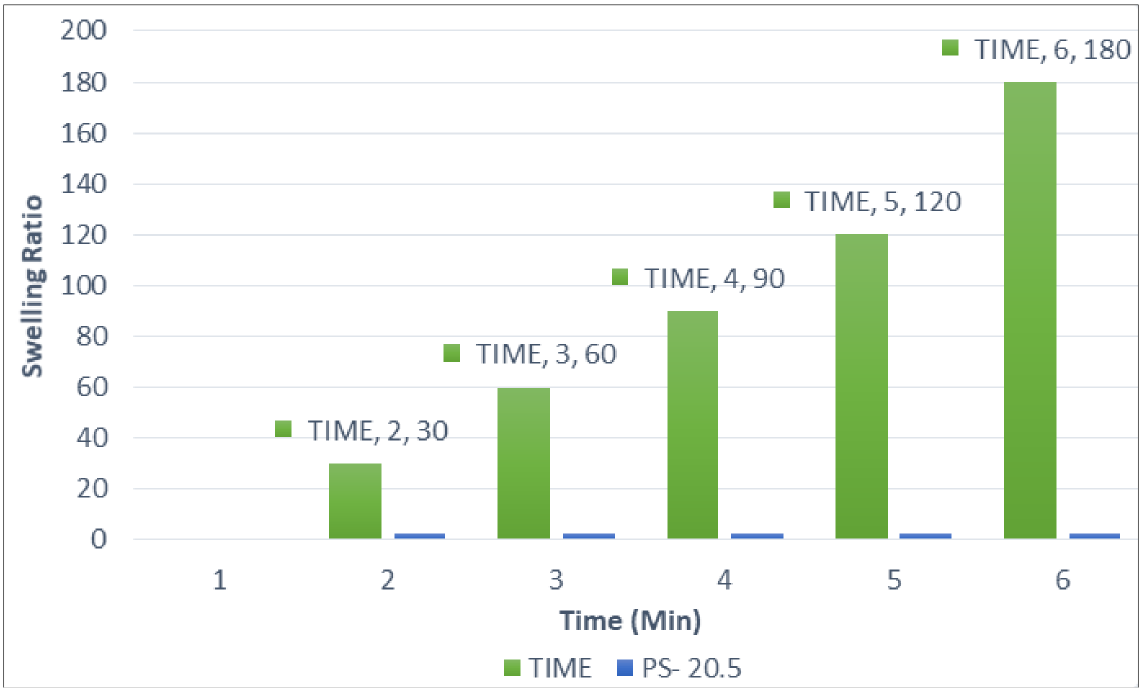

Fig 3: Effect of concentration of PVA- starch blends on the swelling ratio at the fixed composition PVA = 2g and Starch = 0.5 g

2.5.2 Effect of PVA - In present investigates the influence of PVA content in the blends on the swelling ratio studied. Results are shown in Figure 4. (Table-2). Which clearly depict the that the swelling ratio increased while a fall in degree of water sorption is noticed beyond it.

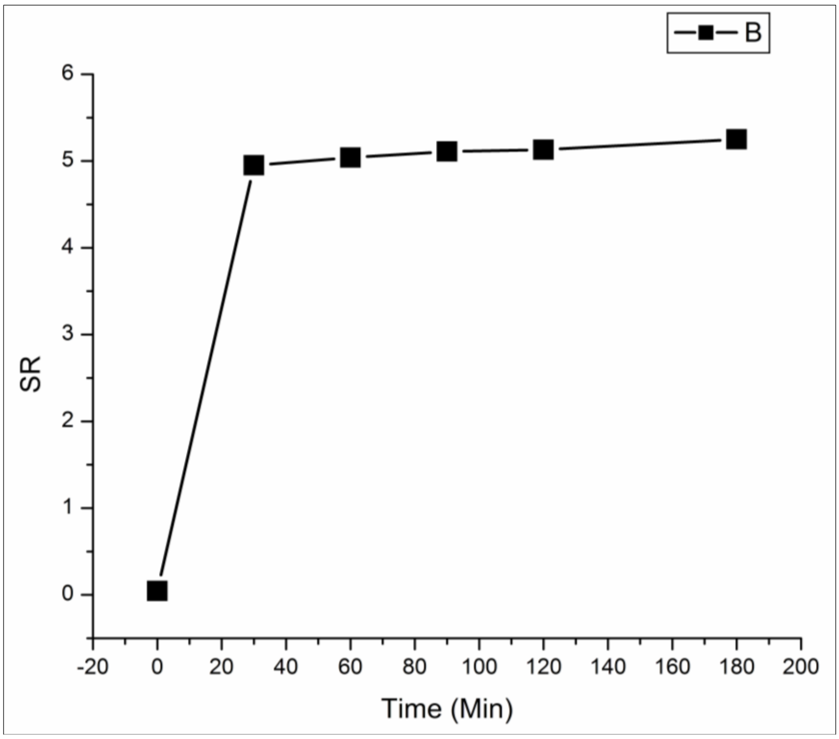

Fig 4: Effect of concentration of PVA

3. Results and Discussion

The sorption data can be mechanistically analyzed on the basis amount of water absorbed (uptake) as function PF time. In present study, the effect of increasing concentration of starch on the swelling behaviors of blends has been observed by polymerizing of starch in mixture is in increasing concentration starch. The influence of PVA content in the blends on the swelling ratio studied. The swelling ratio increased while a fall in degree of water sorption is noticed beyond it.

4. Conclusion

Have explored the possibility of the preparation of novel biopolymers. Starch is a widely used biopolymer; work has to be done on the swelling behaviour of these polymers and physiological effect. Theoretically all the components of the system are biodegradable and thus do not pose any health hazards.

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