APPLICATION OF ORANGE PEEL BIO-NANOCOMPOSITES AS ENCAPSULANT IN MICROENCAPSULATION

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ABSTRACT

Paprika Oleoresin (PO) is a widely used natural colour in the food industry and microencapsulation by spray drying has served to be a successful option to prevent colour degradation of these compounds. This research was focused on evaluating the enhancement of physicochemical properties by using a blend of Gum Arabic (GA) and Orangepeel nanofibers (OPNF) as encapsulants. The addition of nanofibers to polymers resulted in superior properties, characterised by mechanical properties and SEM analyses. The wall material (GA:OPNF) was tested for different proportions (50:50, 60:40, 70:30, 80:20) by comparing encapsulation efficiency and moisture content. The best encapsulation efficiency was exhibited at 80:20 but moisture content was lowest at 70:30. Hence the latter was chosen for the evaluation of physicochemical properties such as water activity, hygroscopicity, caking, solubility, density, flowability and colour. The outcomes suggest that the proposed nanomaterial from orangepeel could serve as a potential supplement to the conventional encapsulant.

KEYWORDS

Bio-nanocomposite, Orange Peel Nanofibers, Microencapsulation, Spray drying, Paprika oleoresin

1. INTRODUCTION

Colour is a crucial visual characteristic of a food product that has a direct effect on the aesthetic value, sensory acceptability, safety and choice of the food product by the consumer [1]. In recent years, there has been a shift in demand towards natural colourants that are now preferred over synthetic ones, especially because of the increasing consumer consciousness towards natural products driven by safety issues and the nutraceutical properties that the natural antioxidants in the compounds provide [2] [3]. Paprika oleoresin is an oil-soluble material extracted from pepper fruits (*Capsicum annuum* L.) mainly composed of carotenoids, glycerides and polyphenolic antioxidants, making it a suitable natural colourant during food processing [4] [5]. It finds application as a natural colourant either to correct or reinforce colour in foodstuffs or as a flavouring substance [6]. All carotenoid pigments have a polyenoic chain as a structural feature, and this chain is what gives them their physical and chemical characteristics, biological functions, colouring and antioxidant activities [4]. Despite their colouring properties, the carotenoids in paprika oleoresin also offer several therapeutic benefits by preventing the occurrence of chronic diseases like cancer, diabetes, cardiovascular problems and obesity [7].

However, the carotenoids are prone to degradation by external factors, causing high instability during storage of these compounds. The strong pungency, poor solubility in water and low stability at different temperature and pH conditions, limits its application in food products [8] [7]. Even though all of the beneficial features of carotenoid pigments are due to their polyenoic structure, this also renders them extremely susceptible to light, heat and prooxidant environments, which can encourage oxidation of the pigments, in turn, affecting the shelf life [4] [5]. Hence, this high instability of the compounds brings in the necessity of a stabilization process to preserve their original colour and potential health benefits [2]. These drawbacks of instability could be overcome by emulsification or encapsulating the pigments with suitable carrier agents, which will protect them from degradation and also improve the bioavailability of the compounds [9]. Microencapsulation is a promising technique in the domain used in the food industry. It is defined as the process of coating or covering ingredients in other material matrices or the incorporation of compounds in a matrix to obtain small capsules of 1 to 1000 microns in diameter. During the encapsulation process, a microenvironment is established within the materials, which hinders contact with the outside atmosphere, thereby keeping the bioactive compounds from degrading, inhibits the oxidation process, prevents colour degradation and prolongs the functional life of the materials [10]. Although the controlled release of the active material at the correct place, timing and rate, as well as preservation of the bioactive components from the external environment are the key goals of encapsulation, there are also other advantages that the technique delivers such as thermal stability, protection of volatiles from unstable and hostile media masking of unwanted odours, flavour or taste, low cost, less toxicity and better nutritional bioavailability [11] [12]. There are several methods that have been used to encapsulate materials, but Spray drying is the widely used one in the food industry due to its comparative superiority over other encapsulating techniques. Spray drying method of microencapsulation offers benefits such as low cost of production, minimal energy consumption, availability of equipment, continuity, flexibility, wide choice of carrier agents, rapid solubility, good stability and quality of the finished product [13] [3] [14] [9]. In addition, spray drying is considered an ideal method for encapsulating oils and oleoresins and particularly heat-sensitive ingredients, as the drying process is very rapid [6] [15]. One of the major benefits of spray drying is that it can produce powder particles with low moisture content and water activity, which in turn will contribute to increased stability and shelf life [8]. As the process entails instantaneous heat transfer from the air to the droplets, there will be minimal deterioration of the components [16].

Gum Arabic or Gum Acacia (GA) is a hydrocolloid obtained from the natural exudate of the stems and branches of acacia trees, consisting mainly of high molecular weight polysaccharides like galactose, rhamnose, arabinose and glucuronic acid [13] [15]. It has been demonstrated to be the most efficient carrier for spray drying when it comes to encapsulating volatiles or hydrophobic compounds because of its bland flavour and the ability to form a stable emulsion and retain volatiles effectively [3]. It is also characterized by high water solubility (up to 50%), the capability of forming films, low viscosity of concentrated solutions compared to the other hydrocolloid gums and good emulsifying properties which can impart high encapsulation efficiency during spray drying [4] [13] [8] [15]. GA is reported to be ideally suitable for encapsulating lipid droplets, especially actives like paprika oleoresin, as it does the role of both surfactant and drying matrix, thereby preventing the loss of volatile compounds [13]. However, gum arabic's use as the sole wall material for encapsulating food ingredients has been limited because of its higher cost of production and limited availability compared to alternative carbohydrate-based materials [11] [16]. Therefore, there is a need to blend it with other wall materials to reduce the cost of encapsulation. Furthermore, based on the structure and properties of the shell materials, the employment of multiple carrier agents for powder manufacture might result in varying physicochemical qualities of the product such as moisture content, water activity, hygroscopicity and solubility [3]. Besides, the starch-based films generally possess poor mechanical properties, while mechanical properties are important for all applications.

Hence, the development of polymer blends with greater encapsulating efficiency and cheaper cost than individual biopolymers is a necessity and this has been an object of research significance in recent times.

The advancement in the field of Nanotechnology has resulted in the creation of a new generation of nanostructured hybrid materials forming a new class known as nanocomposites. Bio-nanocomposites (BNCs) are composite materials generally produced by incorporation of nanomaterials into biopolymers, that have gained much attention in this age due to their renewability, biodegradability, biocompatibility, cost-effectiveness, thermal stability, mechanical and barrier properties [17] [18] [19]. Several studies prove that these nanomaterials can enhance the mechanical, thermal and barrier properties (water vapour and oxygen permeability) and thus serve as reinforcement agents [20]. Till now, they have been progressively utilized in applications such as edible, eco-friendly packaging films, prebiotic encapsulation matrices, conductive polymers, super-adsorbent materials and biomedical applications like drug encapsulation or drug-delivery systems, vaccination, wound dressings, bone regenerating and gene repair treatments, tissue engineering, hydrogels and so on [17] [21]. In this regard, there has been a lot of research going on in the past decade to produce novel bionanocomposite materials and finding advanced applications of BNCs is an area that holds vast innovative prospective. Cellulose nanofibers (CNF) generated from agricultural wastes or byproducts, have recently been added to the choice of nanoscale reinforcement in composites. Thereby, the process becomes extremely efficient, cost-effective and sustainable as the material is abundantly available and it allows for valorising food processing waste. They possess high crystallinity, high modulus, high surface area and perform as ideal fillers for polysaccharides due to their compatibility and comparable chemical structure [22].

In this study, nanofibers derived from orange (*Citrus sinensis*) peel are chosen as the nanofiller. Orange peel nanofibers (OPNF) are isolated from orange peel biomass, which are lignocellulosic sources, using acid hydrolysis by strong acids like H_2SO_4 or HCl followed by high-pressure homogenisation [18]. Citrus fruits such as oranges are one among the agricultural crops that generate surplus amounts of waste worldwide during the processing of the fruits into value-added products like juices, jams, squashes, marmalades or jellies [23]. Thus, the utilisation of OPNF from orange peel residue not only enhances the encapsulation characteristics but contributes to the reduction of agro-waste build-up in the environment as well. On that account, this research is focused on producing a novel bio-nanocomposite material from gum arabic and orange peel nanofibers and utilising it as a coating material in the encapsulation of paprika oleoresin. When compared to the natural matrix polymers commonly used for encapsulation of the natural colour in the food industry, the ability of the materials produced as a result of nanofiber inclusion to enhance mechanics and other physicochemical properties of the powders are tested.

2. MATERIALS AND METHODS

2.1. Materials

Orange peel nanofibers, Paprika oleoresin of 1,70,000 CU, Gum Arabic (food grade) and the required chemicals (glycerol, water, acetone, NaCl) were obtained from Plant Lipids Pvt Ltd., Kerala.

2.2. Preparation of Bio-Nanocomposites

All the membranes were fabricated using the solvent casting technique. In the first step, the polymer Gum Arabic, was weighed using a weighing balance (Kern, KB 2000-2N, Germany) and

suspensions were made in various ratios to get the required consistency. GA was mixed in hot distilled water at 60-70˚C by heating in a water bath and continuous vigorous stirring until the polymer got completely dissolved. Glycerol (20 weight % on a dry basis) was added to the solutions as plasticizer. Then Orange peel nanofibers were added up to the mixed solutions at different concentrations (2%, 4%, 6% and 8%) and mixed thoroughly in a high shear mixer (Ystral, X 10/20-E3, Germany) at 3000 rpm for 10 min. The prepared membrane solutions were sonicated in an ultrasonic bath sonicator (PCI Analytics, PCIAE-07, Mumbai, India) for 20 min and then poured in 20 ml quantity to ensure uniform thickness onto clean and sterile Petri dishes previously coated with glycerol. The plates were marked and then kept in a hot air oven (Binder, ED-S 115, Germany) to dry until the solvent got completely evaporated. A control GA film was also prepared without the addition of OPNF. All nanocomposite films were then stored in dry conditions at 25˚C until used for further testing.

2.3. Characterisation of Bio-Nanocomposites

2.3.1. Mechanical Properties

The mechanical properties of the bio-nanocomposite films with different percent of incorporation of OPNF, viz., tensile strength, Young's modulus and elongation at break were determined in a universal testing machine (Tinius Olsen, H50KT, Noida, India) with a 1 kN load cell. The experiments were carried out using 10 x 5 x 1 mm^3 sample dimensions at room temperature and 500 mm/min cross speed [22].

2.3.2. Surface morphology

Nano structural morphology of the bio-nanocomposite was examined by scanning electron microscope (Tescan, Vega3, Germany) at 15kV accelerating voltage. This was done by placing the samples in aluminum stubs surrounded with double-sided carbon tape and coated with a thin layer of fine gold using a sputter gold coater, to avoid charring [18].

2.4. Preparation of Emulsions for Spray Drying

The emulsions for spray drying were prepared by dissolving PO (core material) into suspensions of wall material (GA + OPNF) in distilled water, such that the total solids reach 30˚Brix. OPNF incorporation was tested in different proportions (50:50, 60:40, 70:30, 80:20 of GA and OPNF). Firstly, the wall materials were dissolved in hot distilled water of 60-70˚C by heating in a water bath. The mixtures were constantly stirred in a high shear mixer until a uniform mix without lumps was obtained and were kept for 12 hours at 4˚C for rehydration. Then, the oil-water emulsions were generated by dosing PO to the solutions in the ratio 1:4 of active material: carrier material and stirred until a uniform bright orange colour was obtained. These are then homogenized in a laboratory homogenizer (APV-1000, USA) at 30/300 psi pressure.

2.4.1. Emulsion stability

The stability of the emulsions was evaluated by a visual determination method, wherein 100 ml of the emulsions were taken in test tubes and stored for 16 hours at 50˚C and later analysed for surface oil [4].

2.5. Microencapsulation by Spray Drying

Microcapsules were produced by feeding the formulations into a High-speed centrifugal spray dryer (LPG-10, Winlong Filling Machinery, China) of 10 kg/hr evaporation capacity and 27 kW

electrical heating power, using a peristaltic pump at 800 ml/h flow rate. The operating conditions were set to 185˚C inlet air temperature, 85˚C outlet air temperature, 350-400 rpm atomizer speed and 44 Hz air flow rate. Spray dried powders were recovered from the collecting chamber, sealed airtight and stored in a desiccator under vacuum with P_2O_5 in such a way as to prevent moisture adsorption, until further testing.

2.5.1. Encapsulation Efficiency

The efficiency of encapsulation was calculated based on the colour value of samples before and after encapsulation and checking for the extent of retainment. The Encapsulation efficiency (EE) was expressed as;

$$\% \text{ EE} = \frac{\text{Colour value of PO in the encapsulated powder}}{\text{Colour value of PO in the feed}} \times 100$$

For determining the colour value, an adequate amount of sample was weighed (approximately 0.3-0.5 g) and dissolved using 10 ml acetone. This was made up to 100 ml using acetone in a standard flask. From this solution, 1 ml sample solution was pipetted out into another 100 ml standard flask, again diluted using acetone and shook well. The absorbance (A) of this solution was measured at 462 nm wavelength, using acetone as blank in a UV-Visible spectrophotometer (Shimadzu, UV-1900i, Japan) [13]. The Colour value was calculated as;

$$\text{Colour value (units)} = \frac{A \times 66000}{W}$$

Where A – Absorbance of the sample at 462 nm
W – Weight of sample (g)

2.5.2. Moisture Content

The encapsulated particles' moisture content was estimated by employing a moisture analyzer at 105 ± 1˚C (Shimadzu, MOC63u, Japan) [8].

2.6. Physicochemical Properties of Microencapsulated Powders

2.6.1. Water Activity

a_w of the microparticles was determined with a water activity meter (Novasina, LabTouch - aw, Switzerland) [14].

2.6.2. Hygroscopicity

For determining the hygroscopicity of the encapsulated powders, 1 g of the samples were loaded in a desiccator with NaCl saturated solution at 75% relative humidity and room temperature and stored until attaining constant weight. The samples were taken out after a week and the weight change was measured. Hygroscopicity was stated in terms of the absorbed moisture in grams per 100 g of dry matter [9].

2.6.3. Degree of Caking

The degree of caking tests was done on the wet samples obtained after determining hygroscopicity. The samples were kept for drying at 102˚C for 1 hr in hot air oven. Once dried,

they were cooled, weight taken and then fed into a 500 µm sieve. The sieve was shaken using a shaking device and then the amount of the particles left was quantified [24]. The degree of caking of the powders was expressed as;

$$\% \text{ Degree of caking} = \frac{b}{a} \times 100$$

Where a – Initial amount of sample
b – Amount of sample remaining on the sieve

2.6.4. Solubility

The solubility of the powders was found by gravimetric method as Water Solubility Index (WSI) [14] [5], where 0.5 g of the samples were first added to 50 ml water and blended. The solution was centrifuged for 5 min at 5000 rpm. The supernatant was collected and 25 ml portion was taken in previously weighed petri plates. The plates were then kept for drying at 105˚C for 2 hours in hot air oven until a constant weight is obtained. Solubility was calculated as;

$$\text{Solubility} = \frac{\text{Dried weight of soluble solids}}{\text{Initial weight of sample}} \times 100$$

2.6.5. Bulk density and Flowability

The Bulk density and Flowability of the encapsulated powders were determined by tapping method using a Tap density tester (TDT 101, ANM Industries, Maharashtra, India). A known weight of sample (W) was taken in the 100 ml graduated cylinder. The volume occupied by it was observed (V_i). The cylinder was then tapped down to a steady value and the final volume recorded (V_f).

Bulk density (ρ_b)of the powders was calculated as;

$$\rho_b = \frac{W}{Vf} \times 100$$

Flowability of the microparticles was calculated based on Hausner ratio (HR) as;

$$HR = \frac{Vi}{Vf}$$

The range of HR values that indicate flowability are 1 - 1.1 for free flowing powders, 1.1 - 1.25 for medium flowing powders, 1.25 - 1.4 for difficult flowing powders and above 1.4 for very difficult flowing powders [24].

2.6.6. Colour

The colour measurements of the spray dried powders were carried out using a spectrophotometer (Konica Minolta, CM-5, Japan). The readings were taken in terms of the CIE parameters ‘L’, ‘a’ and ‘b’ [13].

2.7. Statistical Analysis

All measurements were taken in triplicates and data were expressed as means and standard deviation of three independent measurements.

3. RESULTS AND DISCUSSION

3.1. Characterisation of Bio-Nanocomposites

3.1.1. Mechanical Properties

Figure 1 shows the effects of OPNF content on the three tested mechanical properties; tensile strength, Young's modulus and elongation at break of the composite films. All the films prepared by OPNF incorporation showed superior mechanical properties, high tensile strength and low elongation at break than the control film, owing to the high stiffness of cellulose nanofiber, which indicated reinforcement with the fibers. As the OPNF content was raised from 0 to 6%, there was an increase in the tensile strength from 1.65 MPa to 3.69 MPa. But the value experienced a fall to 3.32 MPa tensile strength when the OPNF concentration was raised to 8%. This result might be due to a reduction in molecular mobility on increasing the OPNF content and decreasing the content of the polymer, which rendered the composites stiff and brittle [18]. A similar trend was detected for Young's modulus as the value increased from 18.19 MPa to 32.56 MPa on increasing the concentration of OPNF from 0% in GA control film to 6% in GA + OPNF 6% film and then decreased to 27.92 MPa for GA + OPNF 8% film, as was expected. However, elongation at break reduced from 62.78% (GA alone) to 42.77% (6% OPNF) and then showed a rise in the value to 44.81% at 8% addition. The result could be attributed to the interfacial tension and formation of hydrogen bonds between the OPNF and GA matrices [22]. The CNF function as a reinforcement agent, forming a good interfacial interaction with the biopolymer matrix, through strong interactions and hydrogen bonding to improve the film's structural and mechanical properties [18] [25]. Hence, the proportion GA + OPNF 6% was finalised as having the best mechanical properties. The results were in good agreement with previous works by Jacob *et al.* (2018) and Gopi *et al*. (2019) that showed the increase in tensile strength and Young's modulus up to 5% addition of Ginger Nanofibers to Potato starch and Tapioca starch films and Turmeric Nanofibers to potato starch, tapioca starch and chitosan films respectively, and further decrease at 7% addition. Similarly, the elongation at break declined up to 5% nanofiber addition, indicating that the mechanical properties showed the peak values at that particular composition [18] [22]. Similarly, Shapi'i *et al*. (2019) studied tapioca starch films reinforced with chitosan and chitosan nanoparticles and found that the addition significantly raised the tensile strength and elongation at break values and the nanoparticle was found to be more effective in improving the mechanical characteristics of starch films than chitosan [25].

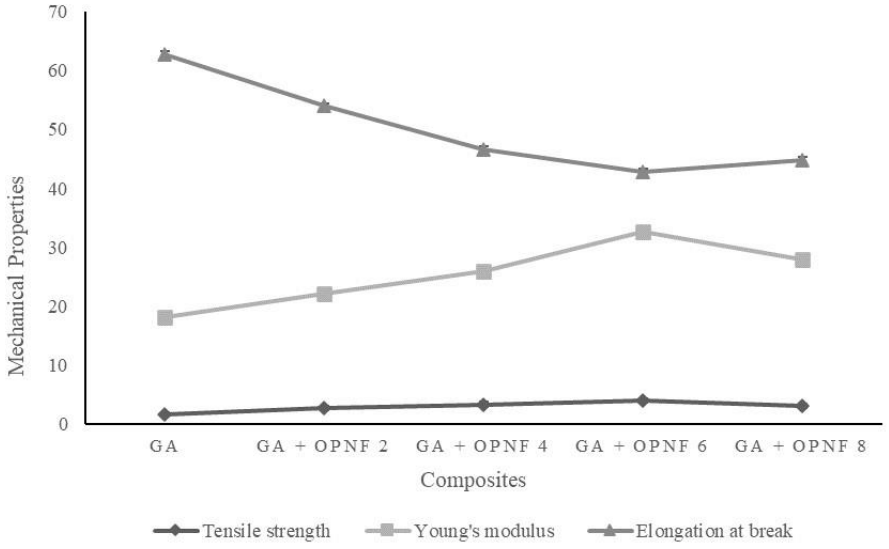

Figure 1. Mechanical properties of composites

3.1.2. SEM Analysis

Figure 2 displays the SEM micrograph of the GA-OPNF bio-nanocomposite film, with 6 weight % of the OPNF. Scanning Electron Microscopy is one of the methods used to authenticate the presence of nanofibers in a matrix. From the image obtained for the film it can be seen that by the incorporation of OPNF to GA, the surface becomes uneven and rough and resulted in tightly packed and aggregated film matrices. In general, if the SEM images of bio-nanocomposites show the presence of large aggregation or clusters, this indicates the presence of strong intermolecular hydrogen bonding between the hydroxyl groups of the polymer and the nanofiber [18]. The SEM image of the composite shows that the OPNF is uniformly dispersed in the GA matrices, which can be owed to the strong electrostatic interactions and hydrogen bonding between OPNF and GA [22]. In addition, the incorporation of OPNF into GA generated higher density composites.

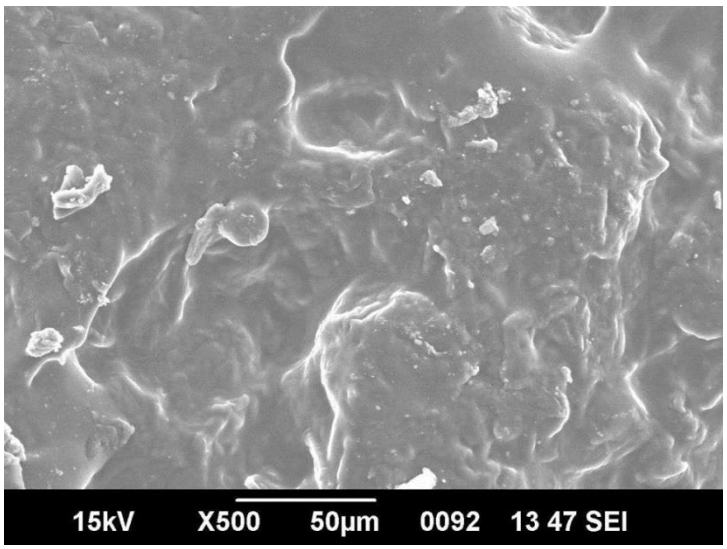

Figure 2. SEM micrograph of (GA + OPNF 6) film at 500x magnification

3.2. Emulsion Stability

The stability visual test of the oil in water emulsions showed no visible oil layer separation, indicating the formation of a stable emulsion of GA and PO. Emulsion stability is an important parameter of microencapsulation because the instability of an emulsion before spray drying can lead to creaming, flocculation and coalescence of droplets after homogenization. All these defects can in turn lead to rupture of the emulsions [4]. The observed result might be attributed to the fact that GA could have acted as a mediator in the production of a stable emulsion by binding both water and oil molecules together and preventing the oil particles from coalescing. From the results for emulsion characterization, it was concluded that the formulations exhibited good consistency across the period under consideration and thus could be spray dried to produce powdered microparticles. In a study conducted by Anthero *et al.*, (2022) to evaluate the efficacy of GA, Octenyl succinic anhydride-modified corn starch and stearic acid-modified malt to form emulsions with PO, they found that the synergism between them, high viscosity and steric forces enabled to produce stable emulsions showing Turbiscan stability index value less than 4.4, which can infer the high stability of emulsions of GA and PO [7].

3.3. Encapsulation Efficiency

The efficiency of encapsulation is a significant parameter to be determined as it denotes the ability of the carriers to retain the active material within it and it can indicate if the pigment degradation could be effectively prevented by microencapsulation. The results in Table 1 show that the efficiency of encapsulation improved by changing the wall material composition, i.e., as the polymer concentration was increased and OPNF concentration reduced. The EE values for PO were within the range of 90 – 96% on using GA-OPNF blend as the coating material. The optimum proportion showing the highest efficiency (96.8608%) was found to be 80:20 of GA and OPNF. Hence, it is clear that the proportions of GA and OPNF affected the EE values and in turn, the bioactive compound's retention, and greater GA concentrations resulted in higher efficiencies. Porras-Saavedra *et al*. (2018) presented the results for encapsulation efficiency as 88.4 ± 1.1% on using a soy protein isolate, maltodextrin, gum Arabic blend (SPI/MD/GA) as carrier agent, compared to 72.4 ± 1.6% in the formulation without GA, implying the role of GA in increasing the efficiency of encapsulation [10]. However, on using MD as the wall material, Díaz *et al*. (2019) obtained encapsulation efficiency as 81.15% for microparticles and a higher efficiency value of 98.50% for submicron particles prepared through nano spray drying [5]. In another study conducted by Anthero *et al*. (2021), the effectiveness of encapsulation after spray drying of PO with GA alone as wall material was 91.82 ± 1.19% [8]. The protein molecules of GA act as surface-active agents to stabilize the oil-water interfaces in homogenization and the air-liquid interfaces in the drying process by forming a coating around the fat droplets [10]. The high hydrophobic nature and good emulsifying properties of GA also additionally contribute to the high PO encapsulation efficiency. Thus, from the findings it can be inferred that the efficiency of encapsulation could be significantly increased by blending the polymer with nanofibers, rather than using the polymer alone. This may be because of the reinforcement ability of the OPNF which increased the strength of the wall material and thereby the ability to hold the core material inside it, more effectively. Besides, GA is a highly branched heteropolymer with protein molecules covalently bonded to the carbohydrate chain, which makes it a good film forming agent and in turn a good encapsulant [3].

Figure 3. Microencapsulated PO powder at proportions 50:50, 60:40 and 80:20 of GA: OPNF

Figure 4. Microencapsulated PO powder at 70:30 proportion of GA: OPNF

3.4. Moisture Content

The results of moisture analysis depicted in Table 1 suggest that the proportion and composition of wall materials have a negative effect on the moisture content of the microencapsulated powders; higher the concentration of polymer, lower the moisture content. But the lowest value was obtained for 70:30 ratio than 80:20, even though the encapsulation efficiency results showed the opposite behaviour. The particular trend for moisture content with changing concentrations of wall material can be owed to the high water-holding capacity of GA. Additionally, as the amount of GA is increased, a polymer network is created, which will increase its chance to entrap more water. As mentioned before, GA contains protein molecules covalently bonded to the polysaccharide moieties. In case of PO encapsulation, these would get embedded in the oleoresin, while the carbohydrates would stretch forth into the aqueous phase from the surface and the PO would impart high hydrophobicity [10]. In this study, the moisture content of PO after encapsulation was observed to be below 5%, specifically in the range of 3.08 - 4.77%, which is characteristic of atomized samples. The obtained results are comparable to the observations by Anthero *et al.* (2021), in which the moisture content of encapsulated PO was 5.74 ± 0.11% [8]. Krithika *et al.* (2014) reported that the moisture content of the paprika powders reduced on increasing the concentration of PO and the value obtained was 5.5% for the formulation containing 15% addition of PO with GA as carrier agent [13]. The moisture content of the encapsulated powders is a critical parameter to consider as a higher level of moisture (above 8%) in powders can affect the physical and chemical stability by leading to the formation of lumps and increase the degree of caking, thereby affecting powder flowability [14]. Low moisture

content is always ideal for storage, handling and ensuring stability of powders. It can indicate the efficiency of the drying process [3] and also influence lipid oxidation and hence the shelf life of the powders [10]. Considering this, the stability of all the tested powder samples can be assured. Literature comparison suggests that the incorporation of OPNF into GA led to the reduction in moisture content of PO powders.

Table 1. Encapsulation efficiency and moisture content of PO microparticles

Encapsulant (GA: OPNF)	**EE (%)**	**Moisture content (%)**
50:50	90.1248 ± 1.6	4.77 ± 0.23
60:40	93.8132 ± 0.91	4.12 ± 0.72
70:30	95.1287 ± 0.77	3.08 ± 0.38
80:20	96.8608 ± 0.25	3.51 ± 0.61

Values expressed as mean ± SD of triplicate determination

Hence, even though the EE was higher for 80:20 proportion of GA: OPNF, the moisture content was found to be lowest for 70:30 proportion. Since the lowest value of moisture content is the ideal criteria for an encapsulated powder more than the encapsulation efficiency affecting powder storage, the 70:30 proportion (PAP ENCAP) was concluded to be the optimum wall material composition for the encapsulation of PO. Further analysis of the physicochemical properties of the powder was carried out in the chosen proportion.

3.5. Physicochemical Characteristics of Encapsulated Powders

The microencapsulated powders must possess certain physical and morphological attributes that are essential for ensuring their stability during powder storage and reconstitution, viz. low moisture content and a_w, decreased hygroscopicity and degree of caking as well as higher flowability and solubility values. The results for the characterization of PAP ENCAP are presented below:

Table 2. Physicochemical properties of PAP ENCAP

Samples	**aw**	**Hygroscopicity (g/100 g)**	**Degree of caking (%)**	**Solubility (%)**	**ρ_b (g/cm^3)**	**HR**
PAP ENCAP	0.148 ± 0.01	13.50 ± 0.51	14.88 ± 0.32	98.62 ± 0.73	0.491 ± 0.03	1.131 ± 0.02

Values expressed as mean ± SD of triplicate determination

3.5.1. Water Activity

The powder produced by spray drying paprika oleoresin with GA and OPNF at 70:30 ratio showed water activity of 0.148 at 24˚C. Water activity has been regarded as one of the most critical quality variables, particularly in the case of long-term storage of food products. It differs from moisture content in the fact that water activity represents the free water available in a food system that is responsible for the biochemical processes like microbial activity or lipid oxidation, while moisture content indicates the total water composition in a food system. An elevated a_w denotes that more free water is present for biochemical reactions, which will affect its shelf life.

The values of a_w in this study signifies that the encapsulated powder is microbiologically stable as microbial growth will not occur below the threshold value of 0.60 [26] and is ideal for storage, handling and prevention of biochemical reactions, mainly lipid oxidation [10]. Rascón *et al*. (2011) studied the storage stability of carotenoids in PO after microencapsulation with GA and SPI at different a_w and found that at a_w above 0.318, the rate of carotenoid degradation increased substantially [4]. Anthero *et al*. (2021) received values for a_w in the range of 0.16 to 0.23 on encapsulation of PO with GA, modified corn starch and pregelatinized waxy corn starch as carrier agents [8] and Porras-Saavedra *et al*. (2018) achieved water activity in the range of 0.17 to 0.24 on encapsulation with employing SPI/MD/GA [10]. However, the water activity value obtained by Díaz *et al*. (2019) was slightly higher (0.465) for powders formed by PO encapsulation using MD [5].

3.5.2. Hygroscopicity

The hygroscopicity value of PAP ENCAP obtained after 1-week storage at 75% RH was 13.50 g H_2O/100 g of total solids. In a study performed by Zhang *et al*. (2019), on the formation of prebiotic xyloligosaccharide particles by spray drying using GA as a carrier, they found similar hygroscopicity values ranging from 13 to 19.87 g of H_2O/100 g [27]. Hygroscopicity can be defined as the potential of a substance to absorb moisture from a higher RH environment [10]. The obtained hygroscopicity values are found to be satisfactory and there was no powder agglomeration, making the samples appropriate for storage, handling and use. The observations in this study match with those made by Anthero *et al*. (2021), who found hygroscopicity value as 13.02 g H_2O/100 g for PO encapsulated with GA alone [8]. Porras-Saavedra *et al*. (2018) achieved hygroscopicity values varying from 11.30 to 12.32% of powder for PO encapsulation by employing SPI/MD/GA as wall materials [10].

3.5.3. Degree of Caking

The degree of caking value for PAP ENCAP is shown in Table 2. The degree of caking is a parameter that has a close relation to the moisture content, water activity and hygroscopicity of the powders and that affects the powder flowability. Caking or clumping of powder particles occurs as a result of inherent or absorbed water content in the powders. When the particles absorb moisture, it forms a saturated solution on the particle surface, making the particle sticky and also forms liquid bridges, which will affect the degree of caking of encapsulated powders [24]. The process of caking begins with the absorption of moisture, followed by the agglomeration of wet particles, which then hinders powder flow. Therefore, low moisture content is essential to prevent caking and thus ensure the stability of the encapsulated powders [3]. Arya *et al*. (2022) reported degree of caking values in the range 11.11 to 14.28% upon encapsulation of fenugreek diosgenin using a blend of MD and whey protein concentrate [24].

3.5.4. Solubility

Solubility is another essential quality feature of powders impacting their functional properties and is referred to as the ability of the powder to dissolve in water or to form a solution or suspension when reconstituted with water [15]. From Table 2 it can be seen that PAP ENCAP showed a high solubility value of 98%. The high water solubility of the powders can be linked with good product reconstitution. Despite PO's hydrophobic nature, the characteristics of GA resulted in particles with high water solubility, and this renders the powders suitable for incorporation into hydrophilic food matrices. Anthero *et al*. (2021) reported powder solubility value of 97.90% for PO encapsulated with GA alone [8].

3.5.5. Bulk density and Flowability

Table 2 shows the results for bulk density and flowability of the powders. The bulk density values for PAP ENCAP were obtained 0.491 g/cm^3. The bulk density of the microcapsules after spray drying is a significant feature that might affect powder packing, transportation and reconstitution. Usually, it is determined by the interparticle space, bulk volume porosity, particle size, shape, density, distribution and moisture content [10]. The bulk density of microencapsulated powders is found to be proportional to the molecular weight of the carrier agents and powder moisture content. When a wall material of high molecular weight is utilised, it fits more easily into the gaps between the particles, taking up less of the total space and yielding greater bulk density values. Besides, the presence of water tends to significantly increase the bulking weight, by increasing their density more than the dry solid [3]. The said trend can be correlated with the findings of this investigation, which indicated that anthocyanin powders had higher moisture content than PO when spray dried. The HR values were found to be 1.131 for PAP ENCAP indicating it to be a medium flowing powder. This result implies that only a small amount of cohesion is present to offer a flowing resistance to the microcapsules. As the flowability entails overcoming surface interactions between powder particles, the surface composition is predicted to have a key impact on the flow behaviour of the spray dried powders. Bulk density values from 0.51 to 0.62 g/cm^3 were obtained by Porras-Saavedra *et al*. (2018) when they encapsulated PO by spray drying using SPI/MD/GA as carrier materials and observed HR values in the range 1.35 - 1.51, thereby concluding it as a powder with poor flowability [10]. Similarly, Krithika *et al*. (2014) determined the bulk density of encapsulated PO with GA in the range of 512.6 to 526.3 kg/m^3 with changing concentrations of PO (5%, 10%, 15%) [13]. When Díaz *et al*. (2019) encapsulated PO with MD, they obtained the HR value as 1.37, which also indicated poor flowability [5].

3.5.6. Colour

The L, a, b values obtained after colour determination are presented in Table 3. Colour is one among the highly critical quality indicators to be tested that can indicate the sensory acceptance as well as pigment retention or degradation after spray drying. Colour measurements using spectrophotometer uses a focused beam of light to measure the energy reflected off the samples over the visible spectrum. L value denotes the lightness (100) to darkness (0) of the product. a and b values denote the chromatic region; a = redness (+) to greenness (-), b = yellowness (+) to blueness (-) [13]. Microencapsulated PO powders were reddish orange in colour, having colour parameters L, a, b as 57.08, 28.54 and 24.94 respectively. The higher value of encapsulation efficiency explains the intense colour in the powders.

Table 3. Colour measurement

Samples	**Colour**		
	L	**a**	**b**
PAP ENCAP	57.08 ± 0.03	28.54 ± 0.12	24.94 ± 0.04

Values expressed as mean ± SD of triplicate determination

4. CONCLUSION

This study explored the use of orange peel nanofibers as reinforcement agents for microencapsulation by spray drying of paprika oleoresin using gum arabic. Amongst the carrier materials examined, the combination of GA and OPNF in the ratio 80:20 led to the highest encapsulation efficiency (96.86%), providing enhanced protection of the pigments. Moisture content of the powders reduced with increasing GA and lowering OPNF content, but the lowest result was observed at GA: OPNF = 70:30 (PAP ENCAP). On evaluating them based on physicochemical properties, all the values were found to be better compared to encapsulation with other wall materials or even GA alone. The powders exhibited low moisture content, water activity, hygroscopicity, degree of caking and bulk density, medium flowability and high solubility. Thus, it was inferred that the GA+OPNF encapsulant act as a better carrier material for encapsulation improving the physicochemical properties of microencapsulated paprika oleoresin. OPNF incorporation into conventional GA encapsulant can be considered as a form of by-product utilisation to valorise the orange peel wastes and also a means to mitigate the problem of high cost and limited availability of GA. Hence, the outcomes of this investigation on the properties of orange peel nanofiber reinforced gum arabic composites as encapsulants suggest the potential to generate a decidedly operational and stable food colouring, thereby providing extensive scope in the food, nutraceutical and pharmaceutical industry.

REFERENCES

[1] M. Paakki, I. Aaltojärvi, M. Sandell, & A. Hopia, (2019) "The importance of the visual aesthetics of colours in food at a workday lunch," *International Journal of Gastronomy and Food Science*, Vol. 16, doi: 10.1016/j.ijgfs.2018.12.001.

[2] S. A. Mahdavi, S. M. Jafari, M. Ghorbani, & E. Assadpoor, (2014) "Spray-Drying Microencapsulation of Anthocyanins by Natural Biopolymers: A Review," *Drying Technolology*, Vol. 32, No. 5, pp. 509–518, doi: 10.1080/07373937.2013.839562.

[3] S. Akhavan Mahdavi, S. M. Jafari, E. Assadpoor, & D. Dehnad, (2016) "Microencapsulation optimization of natural anthocyanins with maltodextrin, gum arabic and gelatin," *International Journal of Biological Macromolecules*, Vol. 85, pp. 379–385, doi: 10.1016/j.ijbiomac.2016.01.011.

[4] M. P. Rascón, C. I. Beristain, H. S. García, & M. A. Salgado, (2011) "Carotenoid retention and storage stability of spray-dried encapsulated paprika oleoresin using gum arabic and Soy protein isolate as wall materials," *LWT - Food Science and Technology*, Vol. 44, No. 2, pp. 549–557, doi: 10.1016/j.lwt.2010.08.021.

[5] D. I. Díaz, E. Lugo, L. A. Pascual-Pineda, & M. Jiménez-Fernández, (2019) "Encapsulation of carotenoid-rich paprika oleoresin through traditional and nano spray drying," *Italian Journal of Food Science*, Vol. 31, No. 1, pp. 125–138.

[6] M. P. Rascón, E. Bonilla, H. S. García, M. A. Salgado, M. T. González-Arnao, & C. I. Beristain, (2015) "T g and a w as criteria for the oxidative stability of spray-dried encapsulated paprika oleoresin," *European Food Research and Technology*, Vol. 241, No. 2. pp. 217–225, doi: 10.1007/s00217-015-2446-6.

[7] A. G. da S. Anthero, T. A. Comunian, E. O. Bezerra, G. de Figueiredo Furtado, & M. D. Hubinger, (2022) "Physicochemical Properties of Capsicum Oleoresin Emulsions Stabilized by Gum Arabic, OSA-Modified Corn Starch, and Modified Malt," *Food and Bioprocess Technology*, Vol. 15, No. 2, pp. 474–485, doi: 10.1007/s11947-021-02728-6.

[8] A. G. da S. Anthero, E. O. Bezerra, T. A. Comunian, F. R. Procópio, & M. D. Hubinger, (2021) "Effect of modified starches and gum arabic on the stability of carotenoids in paprika oleoresin microparticles," *Drying Technology*, Vol. 39, No. 12, pp 1927–1940, doi: 10.1080/07373937.2020.1844227.

[9] Y. A. Begum & S. C. Deka, (2016) "Stability of spray-dried microencapsulated anthocyanins extracted from culinary banana bract," *International Journal of Food Properties.*, Vol. 20, No. 12, pp. 3135–3148, doi: 10.1080/10942912.2016.1277739.

[10] J. Porras-Saavedra, L. Alamilla-Beltrán, L. Lartundo-Rojas, M. de Jesús Perea-Flores, J. YáñezFernández, E. Palacios-González, & G. F. Gutiérrez-López, (2018) "Chemical components distribution and morphology of microcapsules of paprika oleoresin by microscopy and spectroscopy," *Food Hydrocolloids*, Vol. 81, pp. 6–14, 2018, doi: 10.1016/j.foodhyd.2018.02.005.

[11] Y. P. Timilsena, M. A. Haque, & B. Adhikari, (2020) "Encapsulation in the Food Industry: A Brief Historical Overview to Recent Developments," *Food and Nutrition Sciences*, Vol. 11, No. 6, pp. 481–508, doi: 10.4236/fns.2020.116035.

[12] A. B. Sanahuja & A. V. García, (2021) "New trends in the use of volatile compounds in food packaging," *Polymers*, Vol. 13, No. 7, doi: 10.3390/polym13071053.

[13] V. Krithika, S. Radhai, V. Thirupathi, & R. Naik, (2014) "Microencapsulation of Paprika (Capsicum annum L) Oleoresin by Spray drying," *International Journal of Scientific and Engineering Research*, Vol. 5, No. 2, pp. 971–980.

[14] A. Kalušević, S. Lević, B. Čalija, M. Pantić, M. Belović, V. Pavlović, B. Bugarski, J. Milić, S. Žilić, & V. Nedović, (2017) "Microencapsulation of anthocyanin-rich black soybean coat extract by spray drying using maltodextrin, gum arabic and skimmed milk powder," *Journal of Microencapsulation*, Vol. 34, No. 5, pp. 475–487, doi: 10.1080/02652048.2017.1354939.

[15] Q. D. Nguyen, T. T. Dang, T. V. L. Nguyen, T. T. D. Nguyen, & N. N. Nguyen, (2022) "Microencapsulation of roselle (Hibiscus sabdariffa L.) anthocyanins: Effects of different carriers on selected physicochemical properties and antioxidant activities of spray-dried and freeze-dried powder," *International Journal of Food Properties*, Vol. 25, No. 1, pp. 359–374, doi: 10.1080/10942912.2022.2044846.

[16] A. S. Patel, A. Kar, & D. Mohapatra, (2020) "Development of microencapsulated anthocyaninrich powder using soy protein isolate, jackfruit seed starch and an emulsifier (NBRE-15) as encapsulating materials," *Scientific Reports*, Vol. 10, No. 1, pp. 1–12, doi: 10.1038/s41598-02067191-3.

[17] R. Zafar, K. M. Zia, S. Tabasum, F. Jabeen, A. Noreen, & M. Zuber, (2016) "Polysaccharide based bionanocomposites, properties and applications: A review," *International Journal of Biological Macromolecules*, Vol. 92, pp. 1012–1024, doi: 10.1016/j.ijbiomac.2016.07.102.

[18] J. Jacob, J. T. Haponiuk, S. Thomas, G. Peter, & S. Gopi, (2018) "Use of ginger nanofibers for the preparation of cellulose nanocomposites and their antimicrobial activities," *Fibers*, Vol. 6, No. 4, doi: 10.3390/fib6040079.

[19] R. Sharma, S. M. Jafari, & S. Sharma, (2020) "Antimicrobial bio-nanocomposites and their potential applications in food packaging," *Food Control*, Vol. 112, pp. 107086, doi: 10.1016/j.foodcont.2020.107086.

[20] H. Tibolla, F. M. Pelissari, J. T. Martins, E. M. Lanzoni, A. A. Vicente, F. C. Menegalli, & R. L. Cunha, (2019) "Banana starch nanocomposite with cellulose nanofibers isolated from banana peel by enzymatic treatment: In vitro cytotoxicity assessment," *Carbohydrate Polymers*, Vol. 207, pp. 169–179, doi: 10.1016/j.carbpol.2018.11.079.

[21] B. Arora, R. Bhatia, & P. Attri, (2018) "Bionanocomposites: Green materials for a sustainable future," in *New polymer nanocomposites for environmental remediation*. Elsevier Inc, pp. 699712, doi: 10.1016/B978-0-12-811033-1.00027-5.

[22] S. Gopi, A. Amalraj, S. Jude, S. Thomas, & Q. Guo, (2019) "Bionanocomposite films based on potato, tapioca starch and chitosan reinforced with cellulose nanofiber isolated from turmeric spent," *Journal of the Taiwan Institute of Chemical Engineers*, Vol. 96, pp. 664–671, doi: 10.1016/j.jtice.2019.01.003.

[23] D. B. Menezes, F. M. Diz, L. F. Romanholo Ferreira, Y. Corrales, J. R. Baudrit, L. P. Costa, & M. L. Hernández-Macedo, (2021) "Starch-based biocomposite membrane reinforced by orange bagasse cellulose nanofibers extracted from ionic liquid treatment," *Cellulose*, Vol. 28, No. 7, pp. 4137–4149, doi: 10.1007/s10570-021-03814-w.

[24] P. Arya & P. Kumar, (2022) "Characterization of spray dried diosgenin from fenugreek using binary blend of carrier agents," *Applied Food Research*, Vol. 2, No. 1, pp. 100054, doi: 10.1016/j.afres.2022.100054.

[25] R. A. Shapi'i, S. H. Othman, M. N. Naim, & R. K. Basha, (2019) "Mechanical properties of tapioca starch-based film incorporated with bulk chitosan and chitosan nanoparticle: A comparative study," *Pertanika Journal of Science and Technology*, Vol. 27, No. S1, pp. 95–107.

[26] C. Yamashita, M. M. S. Chung, C. dos Santos, C. R. M. Mayer, I. C. F. Moraes, & I. G. Branco, (2017) "Microencapsulation of an anthocyanin-rich blackberry (Rubus spp.) by-product extract by

freeze-drying," *LWT - Food Science and Technology*, Vol. 84, pp. 256–262, doi: 10.1016/j.lwt.2017.05.063.

[27] L. Zhang, X. Zeng, J. Qiu, J. Du, X. Cao, X. Tang, L. Sun, S. Li, T. Lei, S. Liu, & L. Lin, (2019) "Spray-dried xylooligosaccharides carried by gum Arabic," *Industrial Crops and Products*, Vol. 135, pp. 330–343, doi: 10.1016/j.indcrop.2019.04.045.