Review

Interactome of millet-based food matrices: A review

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A B S T R A C T

Millets are recently being recognized as emerging food ingredients with multifaceted applications. Whole grain flours made from millets, exhibit diverse chemical compositions, starch digestibility and physicochemical properties. A food matrix can be viewed as a section of food microstructure, commonly coinciding with a physical spatial domain that interacts or imparts specific functionalities to a particular food constituent. The complex millet-based food matrices can help individuals to attain nutritional benefits due to the intricate and unique digestive properties of these foods. This review helps to fundamentally understand the binary and ternary interactions of millet-based foods. Nutritional bioavailability and bioaccessibility are also discussed based on additive, synergistic, masking, the antagonistic or neutralizing effect of different food matrix components on each other and the surrounding medium. The molecular basis of these interactions and their effect on important functional attributes like starch retrogradation, gelling, pasting, water, and oil holding capacity is also discussed.

1. Introduction

The nutritional quality of food is the primary determinant of human health and physical wellbeing. Maintenance of optimum physical health is the driving force for the advancement and expansion of human genetic potential. Crops endowed with the ability to resist adverse climatic conditions and climate change, along with high nutritive values can successfully address the issue of nutritional and food security, especially in developing nations (Jukanti et al., 2016). Economic viability, fewer inputs, resistance to climate change and superior nutritional quality has increased the importance of millets more than ever in this 21st century (Tomar, Bhardwaj, Kumar, Pal Singh, et al., 2021; Tomar, Bhardwaj, Kumar, Singh, et al., 2021). Millet is a generic term that includes several small grain species, belonging to the grass family *Poaceae/ Gramineae* and were used as a source of food and nutrition for more than 10,000 years (Lu et al., 2009). The four types of major millets include pearl millet (*Pennisetum glaucum*), foxtail millet (*Setaria italica*), finger millet (*Eleusine coracana*) and proso millet or white millet (*Panicum miliaceum*). Minor millets comprise of kodo millet (*Paspalum scrobiculatum*), little

millet (*Panicum sumatrense*), barnyard millet (*Echinochloa* spp.), fonio (*Digitaria exilis*), teff (*Eragrostis tef*), browntop millet (*Panicum ramosum* or *Brachiaria ramose* or *Urochloa ramosa*) and Guinea millet (*Urochloa deflexa = Brachiaria deflexa*) (Amadou et al., 2013).

Millets are categorized as "*Nutri-cereals*" due to the rich content of proteins with balanced amino acids, minerals, fibre, fatty acids, carbohydrates and antioxidant phytochemicals. This makes millets a suitable candidate for processing and as an ingredient in diversified foods especially in gluten-free functional products (Dias-Martins et al., 2018). Owing to such superior nutritional attributes, millets have been used for making traditional/common food products like flat breads, porridges, alcoholic and non-alcoholic beverages, sweets, pasta, cakes, cookies puffs other than functional food products (Adebiyi et al., 2017). Pearl millet grains can be viewed as a potential substitute for food diversification due to their superior nutritional attributes compared to other cereal grains like maize, wheat and rice (Taylor, 2016). The proximate chemical constitution of pearl millet grains on a dry weight basis includes 11.80 g/100 g protein, 72.20 g/100 g carbohydrate, 7.80 g/100 g dietary fibre, 6.4 g/100 g lipid, 1.8 g/100 g minerals (Adebiyi et al.,

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2017). Even though such proximate composition studies are available, limiting reports exist on deciphering a clear understanding of the molecular interactions among the food matrix components in pearl millet and other millets.

It is widely known that millet based foods are diverse in the composition of nutrients like carbohydrates, fats and proteins, and other minor components (salt, vitamins, sodium, calcium and iron, additives, etc.) (Tomar, Bhardwaj, Kumar, Pal Singh, et al., 2021). What is less known is that these nutrients are neither homogeneously dispersed nor present in a free form, but as a portion of complex microstructures (Mondal et al., 2022). Food structure and its relation with desirable nutritional, sensorial, and physical properties, and derived health implications has recently been an important research area. The nutrients are integrated into a continuous cellular medium of natural origin or in microstructures produced by food processing, known as *food matrix*. Food scientists and nutritionists have recognized that the microstructural organization and food matrix rather than the chemical composition dictate the textural responses, functional properties and nutritional quality of food products.

As millets are considered effective staples to address nutritional security, it is vital to unravel the bioaccessibility and ultimate bioavailability of their nutrients. The bioaccessibility of millet based foods (the portion of the ingested nutrient or bioactive compound released from the food matrix in GIT) (Carbonell-Capella et al., 2014) and bioavailability (the portion of the ingested nutrient or bioactive compound that enters the systemic circulation) (Motilva et al., 2015) directly relies on their nutritional composition and molecular interactions between the food matrix components and their interactions. Nutrient bioavailability is the ultimate indicator of quality and relies on the type of food matrix, its discharge from the matrix, chemical changes during digestion, uptake mechanism, biodistribution and metabolism. *In-vitro* methods to evaluate bioavailability/bio-accessibility can help to decipher the molecular interactions between food components and nutrients, the influence of enzyme activity, pH, processing and food preparation on the absorption of nutrients or biomolecules (Sandberg, 2005). *In-vitro* dialysis, dynamic or static gastrointestinal models are extensively being used to analyze the bioavailability/ bioaccessibility of phytonutrients (Santos et al., 2019). Different physiological processes are accountable for the decrease in nutrient bioavailability. These processes include decreased solubility or generation of insoluble complexes in the GIT, lower nutrient release rate from the food matrix, decreased permeability across the intestinal mucus layer and molecular transformations of nutrients (Thakur et al., 2020).

Physicochemical properties of millet-based foods are influenced by the accessible reactive groups and the unmasking of their hydrophobic regions in a given medium. Thus, the functional properties exhibited by a system at a given pH and water activity, at a specified temperature range, can be primarily predicted by the structure and interactions of its respective lipids, proteins and saccharides in a particular food matrix. Physicochemical interactions between the food matrix components primarily govern the generation of gels, foams and emulsions. They influence the sensory qualities of food, shearing resistance, and the flow of the material in the processing equipment. Evaluation of the functional properties of millet-based food regarding food component interactions can expedite the development of functional food products and nutraceuticals of the desired quality. These properties can also be enhanced by intentional chemical and enzymatic modifications of the biomolecules, that modify the hydrophobic or hydrophilic character, size, charge density or by changing the environment.

Interactions between food matrix components present in a specific food formulation dictate their molecular assembly over multiple length scales and consequently the final structure of food products, thus influencing the texture, nutritional and functional aspects of the foods. These matrix component interactions are classified into binary, ternary and quaternary interactions. With respect to millet based foods, the food matrix interactions like binary (starch-lipid, starch-protein, lipid-

protein, macromolecules-minerals/phenols/vitamins/colourants), ternary (starch-lipid-protein) interactions have been observed. These matrix interactions fundamentally govern various physicochemical properties including starch gelatinization, retrogradation, sensory and processing qualities, gel formation, water and oil holding properties, farinographical, tensile properties, viscosity, pasting, and textural properties) and nutritional quality traits including starch, protein and lipid hydrolysis, digestibility, glycaemic potential, nutrient bioavailability and bioaccessibility etc. To date, limited studies have addressed the potential role of these humble grains. In this review, we comprehensively elaborate and conceptually explain various food matrix components, the molecular basis of their physicochemical and biochemical interactions with respect to nutritional bioavailability, functional properties and the development of novel food products.

2. Concept of food matrix: Relevance in understanding nutritional quality

Understanding the food matrix at a molecular level to decipher how food components interact is critical for the ultimate food quality. These interactions also follow the fundamental laws of physics and chemistry, regardless of where they occur and can be both thermodynamically and kinetically characterized. Nevertheless, when these chemical interactions occur in actual foods, in some cases distinct results are obtained when compared to the same interaction taking place in aqueous solutions. This is because food does not act as an ideal solution. Food is a concentrated, multicomponent and intricate system containing components like lipids, proteins, minerals, flavours, colourants, carbohydrates and other functional compounds which constitute the food matrix and can exist in variable physical states (Fig. 1B). Since food does not act as an ideal solution, molecular interactions between the food matrix components add a higher level of complexity, chiefly to understand the inhomogeneous signals (contributed by components) due to their unpredictable molecular configurations within the matrix. Tagging matrix components using visual markers within the matrix could reveal their complex association in a stage/state-specific manner.

With respect to millets, the "Matrix" is something where the components are nested or embedded and their functionality could be delineated in terms of diffusivity, strength, stability and scaffolding. In the light of nutrition and food science, "matrix" is referred to as the effective food which is composed of a nutrient or their blend which are either naturally or artificially included. Millet based foods have a diverse and complex labyrinth composed of macro and micromolecules. The food matrix is often confused with the food microstructure and is viewed as the structural organization of different food components at multiple spatial length scales (Capuano et al., 2018). Food matrix in millets is a part of food microstructure that typically corresponds to a spatial and physical domain that include, interacts directly and/or imparts a specific functionality to a matrix component (nutrient) or food element. The food matrix is component-specific as different structural elements in the same food may interact with different matrices.

3. Different types of food matrix interactions

Matrix of functional foods based on millets has an inconstant, irregular and complex structure containing components like lipids (1.43 to 6 g/100 g), protein (10 to 11 g/100 g), minerals (1.7 to 4.3 g/100 g), carbohydrates (56.88 to 72.97 g/100 g), which are inherently topped with flavours, colourants and other functional compounds. In millets, this complex system contains several ubiquitously present molecular interactions like electrostatic, hydrophobic, hydrogen bonding, π-π stacking, and coordination forces. In millet based foods, these interactions can either cause undesirable effects like reduced stability and solubility or lead to a desirable enhancement in the functionality and quality of food (Patel et al., 2013). It has been proved that the interaction between the matrix components in millet based food formulations,
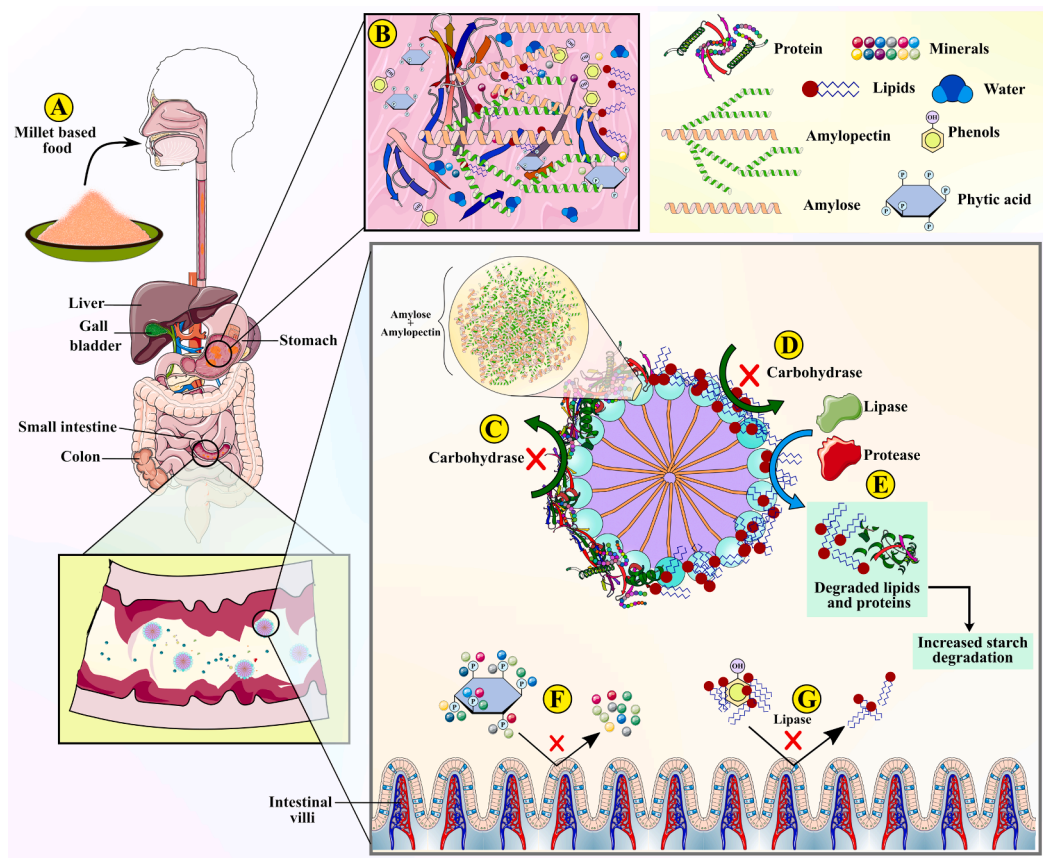
Fig. 1. Indicates the different types of food matrix interactions; A) Ingestion of pearl millet-based food products; B) Food matrix containing starch, proteins, phenols, phytic acid, lipids, minerals and water; C) Impediment of starch degradation by carbohydrases due to complex formation between starch and lipid molecules; D) Impediment of starch degradation by carbohydrases due to complex formation between starch and proteins; E) Disintegration of lipids and proteins by lipase and protease respectively increases the accessibility of carbohydrases to starch granules. This increases the starch digestion; F) Chelation of essential cations like Potassium, Zinc, Copper, Iron, Magnesium and Calcium by phytic acid decreases the mineral bioavailability, causing their deficiency; G) Polyphenols reduce fat absorption by interacting with lipids in the food matrix and directly inhibiting the lipase activity, affecting health.

dictate their molecular and structural assembly over different length scales and consequently affects the nutritional, textural along with functional aspects (Ai et al., 2015). In the past, it was believed that the structure and composition of the food matrix had a limited effect on food digestion and nutrient bioavailability and the only variable that influenced digestion was the proximate composition of macro/micro-nutrients. Recent attention on the nutritional content of foods is challenged with the fact that several food matrix components or nutrients do not act typically when studied individually than as a part of the whole food system.

Advancement in bromatology has dictated that the millet based foods act like a characteristic pliable, flexible, and soft matter system having multi-phases, multi-components and multiple length scales (Gao et al., 2017). Foods with similar chemical structure and composition display significant variation in nutrient delivery, biological function, the effect on gut microbes and their health effects, highlighting the need to study nutrient transit kinetics and their hydrolysis (Turgeon & Rioux, 2011). This disparity arises from the heterogeneity in interactions between nutrients, food matrix and other components aside from host-related effects (Wahlqvist, 2016). Studies on a single food matrix component to identify the relation between its bioavailability, its spatial arrangement and interaction in the three-dimensional food matrix structure are limited. This is because scientists study a single component of food rather than the whole food to assess their biological effects on animals and cells. Also, the studies on individual components or their mixtures are not found to produce the same effects as whole food due to the complexity of food matrix component interactions. Advancements in

food omics have helped to decipher the effects of some matrix components as an additive, synergistic, masking, antagonistic or neutralizing in millet based foods. Owing to the complexity of these foods the interactions could affect the nutritional bio efficacy or may participate in additional positive effects or negative toxic effects. An additive effect refers to a combination of food and its components that deliver the sum of effects of individual components. A synergistic effect can be defined by an effect that is higher than the total effect of individual components. Antagonism occurs when the total sum of effects is much lesser than the predicted effects of individual components. Masking describes the simultaneous interaction between the components present in a given food matrix leading to a decrease in taste or effect of at least one of the components. Neutralization is referred to as a state when two food matrix components counterpoise each other to produce no effect on the food system.

Naturally occurring macromolecules like polysaccharides and proteins represent the chief categories of millet based food structuring compounds and play a crucial role in providing unique stability and structure to these foods. They are commonly used in food industries for gelling, thickening, as aqueous solutions, for foam stabilization, as dispersions, emulsions, inhibitors of sugar crystal or ice formation, regulators of flavour release and so on in these foods (Williams & Phillips, 2021).

4. Matrix component interactions

Even though matrix characterization and interaction studies are

limiting in processed millet-based functional foods, it is evident that interactions at different scales and dimensions exist. These matrix component interactions are classified into binary, ternary and quaternary interactions.

4.1. Binary interactions

These are specific and non-specific interactions established between two food matrix components resulting from biochemical events which are steered by hydrogen bonds, electrostatic forces, hydrophobic effect. These binary interactions can take place between macromolecules (protein-starch, starch-lipid, lipid-starch, protein-lipid) or between macromolecules and ions (minerals and salts) or macromolecule-small molecules (flavours, colourants, fatty acids, phytochemicals, and vitamins). Since millets have a starch-rich matrix, various starch-lipid, starch-protein and lipid-protein interactions have been observed.

4.1.1. Starch-lipid interaction

Millet-based food contains a dense matrix where starch granules are ensnared in a protein matrix. Lipids like monoglycerides, lysophospholipids and fatty acids form stable complexes with amylose while amylopectin rarely interacts with lipids (Wang et al., 2016). Starch has

the inherent ability to form a helical conformation. These helices may contain a single chain where stabilization is attained by the presence of a guest ligand in the helix lumen. These structures are commonly referred to as 'inclusion complexes'. Starch polymers (amylose and amylopectin) and lipids cause the formation of natural inclusion complexes in native starch or during a heating–cooling protocol, which commonly occurs during food processing. Free fatty acids and saturated monoacyl lipids tend to form helical inclusion complexes with amylose while di- or tri-acyl lipids do not form such complexes. The creation and stabilization of these complexes include several non-covalent interactions like van der Waals forces, hydrophobic attractions, hydrogen bonds (Putseys et al., 2009). The [1 → 4] glucan helices contain hydrophilic hydroxyl groups which are arranged on their outer surface while the oxygens and the methylene groups of the glucosidic bonds line along the inner core shaping a hydrophobic cavity that can accommodate suitable ligands (Fig. 2E). When lipids are legends in the inclusion complex there are commonly six glucosyl residues per helical turn in [1 → 4] glucan helices. Though seven or eight glucosyl units per turn can be formed with other types of ligands.

Studies on starch–lipid complexes using molecular modelling, Raman, nuclear magnetic resonance (NMR) spectroscopy and XRD (X-ray diffraction) indicate that the aliphatic lipid chains are integrated
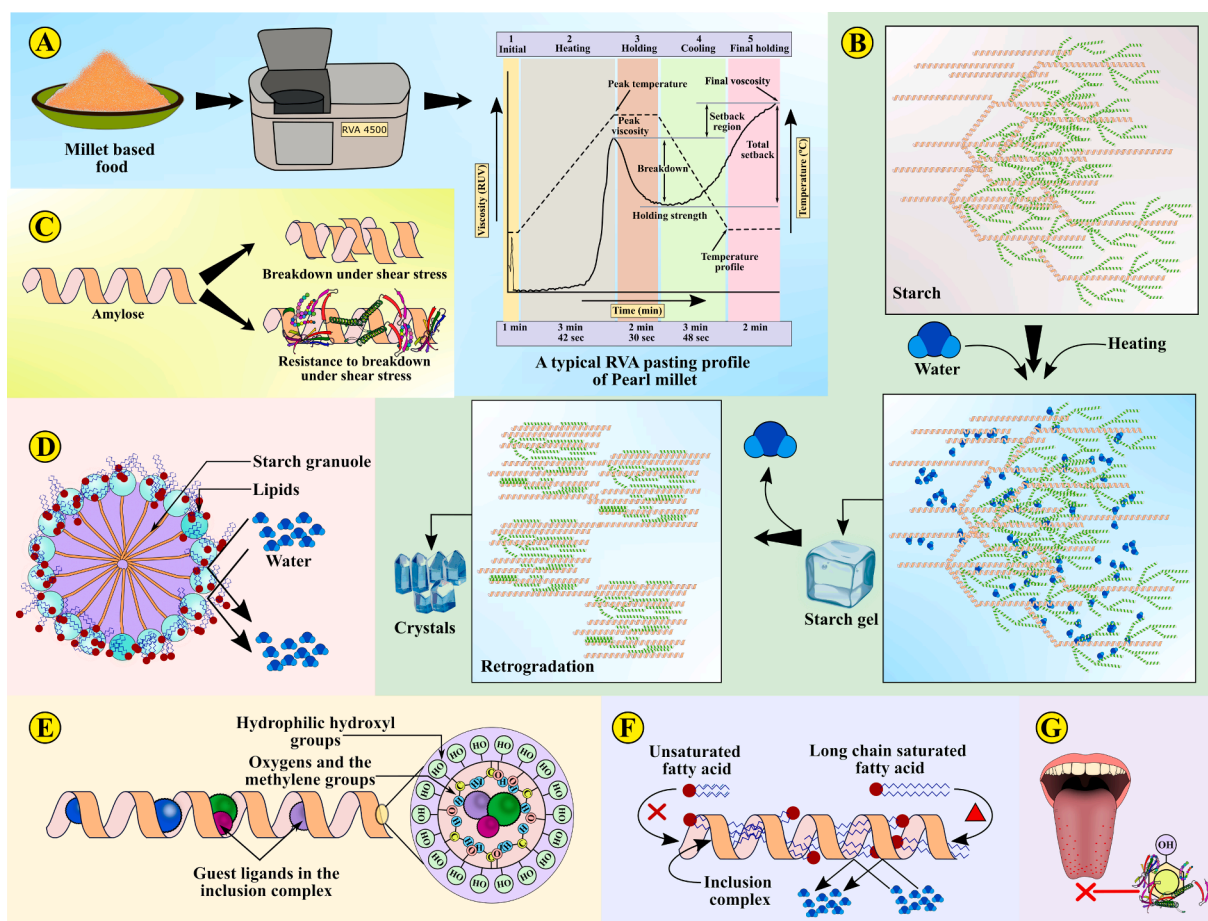
Fig. 2. Depicts the influence of food matrix components on functional properties of millet-based food products. A) A typical RVA (Rapid Visco Analyser) pasting profile for millet-based food; B) Indicates the process of starch gelatinization and retrogradation. Heating starch with water results in the disorganization of crystalline starch granules by a process of gelatinization. During the cooling phase of the amylose in the water/starch mixture, recrystallizes. The process is termed as retrogradation; C) Millet flours exhibit high breakdown values by the adsorption of protein molecules on the exterior surface of the cooked starch molecules, reducing the breakdown under shear stress; D) Complex formation between starch and lipids decreases the peak viscosity and increases the peak temperature by inhibiting the water uptake, reducing the degree of swelling and hydration; E) Formation of a stable complex between amylose and legends assisted by hydrophobic and hydrophilic interactions; F) Influence of lipid chain length and degree of saturation on the formation of starch–lipid complexes. Long chained saturated fatty acids have a higher tendency to form complex with amylose chains while unsaturated fatty acids decrease the complex formation; G) Effect of polyphenol–protein interactions on the astringency sensation of millet-based foods.

into the internal cavity of the amylose helix, while the carboxyl FA (fatty acid) group or glyceride moiety of a monoacylglycerol is revealed on the helix outside, caused by electrostatic repulsions and steric hindrance (Copeland et al., 2009). The helices containing lipids can assemble into crystalline lamellae, where helices are oriented perpendicularly to the plane of the lamellar stacks (Biais et al., 2006). Researchers have proposed that the interspacing amorphous regions and crystalline lamellae are accumulated as micron-sized spherulites.

Since amylose is the chief constituent of starch that forms a complex with lipids, the amylose content in starch chiefly determines the formation of starch–lipid complexes. Contrastingly the lipid-binding capacity of highly branched amylopectin is sufficiently weaker than that of amylose (Wang et al., 2016). An increase in the length of saturated fatty acid chains is positively correlated with the extent of the complex formation while an increase in the degree of unsaturation (double bonds) reduces the complex formation. The inefficacy of di- and triglycerides in forming a stable complex with amylose is directly correlated to the steric hindrance of the molecule which impedes it from entering the polysaccharide helix interior (Fig. 2F).

Complex formation between starch and lipids negatively affects the exposure of starch to specific starch degrading enzymes, lowering its degradation and digestion (Annor et al., 2015). The extent and ease of enzymatic hydrolysis of the superstructures made by amylose–lipid complexes and their degree of organization into helices and aggregated structures made by larger domains of ordered chains have an inverse relation. The initial step of enzyme-mediated hydrolysis of these amylose–lipid complexes involves quick hydrolysis of the amorphous regions of the complex followed by a slower disintegration of the amylose inclusion complex. The chief fatty acids in millets are linoleic, oleic and palmitic acids constituting about 85% of the millet fatty acids (Kawai et al., 2012). Starch complex formation with lauric and oleic acids can effectively reduce the rate of starch hydrolysis while the extent of enzymatic hydrolysis of starch-linoleic acid complexes is similar to that of native starch due to the complex instability (Kawai et al., 2012). Reduction in hydrolysis rates was also evident when high-amylose corn, tapioca, and normal corn starch were mixed with soy lecithin, linoleic acid, oleic acid, stearic acid, palmitic acid and corn oil. The starch hydrolysis rates of starch-lipid complexes varied with the degree of lipid unsaturation (Ai et al., 2013). In a similar study linoleic, oleic and palmitic acids were complexed to cooked foxtail, proso, finger and pearl millet starches and subjected to in vitro starch digestibility and their expected glycemic index (eGI) was calculated. A significant reduction in eGI and in vitro starch digestibility of millet starch-fatty acid complexes was observed. The reduction in the rate of starch hydrolysis was directly related to the quantity of added fatty acids. The unsaturated fatty acids caused the highest decrease in starch hydrolysis especially oleic acid (Annor et al., 2015). A study on *In-vitro* oro-gastro intestinal simulation revealed pearl millet grains to display low inherent glycemic potential (63.71%) compared to that of rice (65.89%) (Mondal et al., 2022). The authors stated that the lipids present in pearl millet grains form complexes with starch. This interaction is based on the swelling and further cracking of gelatinized starch during cooking. This allows the lipid molecules to form a continuous dispersed phase of starch lipid complex in the starch ensnared food matrix. The long hydrophobic lipid tail enters the cavity like structure of amylose facilitating starch to form a stable complex, thereby impeding the accessibility of starch to hydrolytic enzymes.

Pre-cooked foxtail millet starch was subjected to α-amylase treatment (with or without free fatty acids) to study their hydrolysis kinetics (Jin et al., 2019). The independent hydrolysis of starch was 84% after an incubation period of 120 min. On adding free fatty acids, the rate of starch hydrolysis significantly decreased from 82.2% to 71.1%. This reduction in digestibility could result from the helical complex formation between the specific lipids and amylose Fig. 1D. These complexes impede the amylose hydrolysis and also resist the expansion of starch granules, reducing the starch hydrolysis (Ai et al., 2013). The magnitude

of reduction in starch hydrolysis relies on the extent of amylose–fatty acid complex formation.

The extent of starch-lipid interaction also determines their dissociation temperature. The dissociation temperature of the amylose lipid complex (ALC) increases with an increase in the length of the lipid hydrocarbon chain and decrease with an increase in double bonds in these chains (Ai et al., 2013). Foxtail millet with 24.53% starch was subjected to ALC formation with palmitic, oleic and linoleic acid (Jin et al., 2019). The ALC between amylose and palmitic acid showed a high dissociation temperature, due to the strong interaction between the hydrophobic pocket of the amylose helix and the straight hydrocarbon chain of palmitic acid. While the ALC formed between amylose-oleic and amylose-linoleic acid in precooked millet starch exhibited a lower dissociation temperature. This could be due to the weak interaction between the amylose and fatty acid hydrocarbon chain having double bonds.

Heating, in the presence of water, causes disorganization of crystalline starch granules by a process of gelatinization. Amylose is liberated from the granules into the aqueous phase during the gradual expansion of the starch granules. During cooling of water/starch mixture, there is recrystallization of starch (chiefly amylose) by a process termed retrogradation (Fig. 2B). Studies suggest that high amylose content in the food matrix caused a lower insulin and glucose response in humans compared to the one with moderate amylose. Researchers claim that this could be due to the formation of aggregates of slowly digestible amylose and retrograded resistant amylose starch which is resistant to hydrolysis. Also, amylose reacts with lipids in the food matrix reducing the rate of amylolysis due to a reduction in starch swelling. This causes an increase in hydrophobicity, eventually reducing the interaction between enzyme and substrate (Petitot, Abecassis, et al., 2009; Petitot, Brossard, et al., 2009). Also, the granule architecture can greatly influence their hydrolysis. The presence of pinholes and pores in their structure assists the entry and activity of starch degrading hydrolytic enzymes (Kaur et al., 2007). Starch-lipid interaction also affects the pasting temperature of the millet flour (Sharma & Gujral, 2019a, 2019b). The temperature at which the viscosity of a substance starts to increase under heat and is the minimum temperature needed for cooking is termed as pasting temperature. A higher pasting temperature indicates more resistance to disintegration and swelling. Millet flour exhibits a higher pasting temperature than wheat flour. This could be due to the higher fat content in millet flour that exercises a shielding effect by their non-polar groups causing the melting of starch crystals at a higher temperature. The peak viscosity of millet is negatively influenced by starch-lipid interactions (Ragaee et al., 2006). Peak viscosity represents the water-holding capacity of starch or a mixture. The lower peak viscosity of millet flours could result from the formation of an insulating hydrophobic layer of lipids around the starch granule by amylose–lipid interaction, inhibiting the water uptake. Also, the formation of the amylose–lipid complex reduces the degree of swelling and hydration of millet starch, restricting the amylose leaching, reducing the peak viscosity (Singh & Adedeji, 2017). The temperature attained at peak viscosity is called peak temperature and is higher for millet flour when compared with wheat flour (Ragaee et al., 2006). This higher peak temperature in millet starch was due to the process of complex formation between starch and fat molecules, enhancing their granular integrity, suppressing the rise in peak temperature and starch swelling. Interaction between amylose and lipid also reduces the retrogradation of millet starch. This is because the amylose–lipid complex inhibits the mobility and solubility of amylose, hindering recrystallization and network formation (Fig. 2D).

4.1.2. Protein-starch interaction

Interactions between protein and starch have been highly appreciated and conceptualized in making novel functional food formulations like infant foods, bakery products, and desserts, due to their superior nutritional value along with high functionality (Giuberti et al., 2015; Sarabhai & Prabhasankar, 2015). Although protein and starch are

thermodynamically incompatible for stable complex formation, however, their interactions can positively/synergistically influence their individual physicochemical properties (Bakar et al., 2009). The interactions between protein and starch are purely electrostatic. Even though amylopectin and amylose are electrostatically neutral; the granules can attain charge by surface proteins or negatively charged phospholipids. Proteins can attain either a positive or negative charge depending on their amino acid composition and the pH of the surrounding medium (Kumar et al., 2022). Starch granule acts as a negatively charged colloid under a slightly acidic pH, which is commonly found in food systems and forms complex with positively charged proteins (Farmakis et al., 2002). Contrastingly at an alkaline pH, both proteins and starch are negatively charged, preventing the complex formation (Magnusson & Nilsson, 2011). Thus, when starch and proteins are in proximity to a food matrix, they can form a stable complex depending on pH, facilitated by charge-charge, hydrogen bonds and other interactions (Zhen et al., 2022). The extent of wheat starch-protein interaction and their lowest absorption was found at pH 6.5. Also, the interaction of gelatinized wheat starch and protein was higher at low to neutral pH (Dong et al., 2020). Researchers confirm that the maintenance of native protein structure is vital for the formation of starch-protein complexes.

Although a variety of functional foods are prepared from millets due to their high content of dietary fibre (DF) and resistant starch (RS); nevertheless, the lack of gluten and viscoelasticity limits their physicochemical properties. Utilizing millet flours for flatbed preparation requires a supplement to achieve the desired rheological and viscoelastic requirements. Exogenous addition of proteins in millet-based food formulations can improve their sensory quality, texture and storage stability and further reduced starch hydrolysis in the GIT. In a study, millet flours were supplemented with 12% gluten proteins. Results indicated the definite role of these exogenously supplemented proteins in lowering starch retrogradation, improvement in dough development and stability (Sharma & Gujral, 2019a). The lower retrogradation was due to the interactions between gluten and millet starch by hydrogen bonds, lowering the starch recrystallization by altering the molecular redistribution of water (Curti et al., 2014). Glutens and fibres lower down the starch hydrolysis due to their shielding effects against hydrolytic enzymes. Similarly, millet flours exhibit lower dough development time, when compared to wheat flour (Sharma & Gujral, 2019a). The authors explained that the slow hydration rate of wheat gluten, increased the dough development time when compared to millet flours, lacking gluten.

Proteins affect the rate of starch hydrolysis as they form a physical impediment between the degrading enzymes and starches. Proteins like glutenins, globulins and albumins surround the starch granules and form a barrier for amylases. The Interaction of protein with starch in the food matrix limits the surface area for hydrolytic enzyme action, enzyme diffusion, catalysis and consequently impeding starch hydrolysis due to a tightly packed network of protein in a globular starch matrix. Studies on the effect of protein fortification on proso millet in-vitro starch digestibility (IVSD) corroborated this theory (Zheng et al., 2020). They compared the effects of adding zein, soy protein isolate, and whey protein isolate to proso millet flour on starch digestibility and other physicochemical parameters. When the protein was added, there was a considerable difference in starch digestibility. The RS content of protein-millet flour increased from 4.49 per cent to 11.73 per cent, with whey protein isolate having the greatest influence. Congruently, (Ren et al., 2016) also investigated the effect of modifying food matrix components on IVSD and *in-vivo* glycemic index (GI) of foxtail millet flour. A rapid increase in GI and IVSD was observed after deproteination. They claimed a rapid increase in GI and IVSD to the absence of protein-starch complex. A recent study indicated that higher protein content (11.66 %) in pearl millet when compared to that of rice (8.34 %), creates a more complex and tightly packed starch-protein matrix, ultimately reducing the starch hydrolysis (Mondal et al., 2022).

In another study, the addition of rice proteins like prolamin (2.0%), glutelin (5%), globulin (2.5%), albumin (2.0%) were individually added to rice flour reduced the in vitro rice starch digestibility by 6.5%, 10.7%, 6.3% and 8.2%, respectively (Khatun et al., 2020). Similarly, a study was conducted to investigate the interaction between proteins and starch using a model of whey protein isolate-corn starch blends as a model. Reduction in the content of rapidly digestible starch (RDS) and an increase in RS was observed in these blends when compared to native corn starch (Yang et al., 2019). The authors explained that this decrease in vitro starch digestibility could be due to the highly intact protein matrix, impeding the amylolytic activity (Fig. 1C) and starch gelatinization by starch granule entrapment. In the same way, the effect of starch-protein interactions on in vitro starch digestibility and physicochemical properties of potato starch-protein blends were examined. The results indicated that the RDS of the raw starch increased while their RS decreased, the opposite was observed for blends (Lu et al., 2016). Increasing the ratio of proteins, RS and SDS were steadily increased in cooled, cooked or reheated blends indicating the role of proteins as a physical barrier against digestion (Dupuis et al., 2014). In a similar study, the effect of protein on the starch hydrolysis of foxtail millet was investigated by incubating the millet flour with pepsin (for protein removal), before α-amylase digestion (Jin et al., 2019). Pepsin assisted proteolysis of the millet protein matrix relives the starch granules from their entrapment by breaking the protein-starch interactions, increasing the extent and rate of starch hydrolysis and digestibility. The hypoglycemic character of Kodo millet caused by the protein encapsulation of starch granules was also reported (Annor et al., 2013), indicating the role of protein matrix as a physical barrier against starch digestibility.

Since millet starch is a biopolymer containing numerous hydrophilic groups, it can be used for hydrogels preparation. Amino acids can be used as cross linkers for modifying starch by integrating new functional groups into its chains. In a study, Kutki millet starch was isolated and modified with threonine (neutral), aspartic acid (negatively charged), and lysine (positively charged) amino acids at varying pH levels (Mahajan et al., 2021). These modified starches were characterized for their various textural, pasting, structural, and functional properties. It was found that the starch modified with the amino acid at a higher pH showed good textural properties when compared to those at lower a pH. Also, lysine was found to be a better cross linker for modification of Kutki millet starch and preparation of their gels for nutraceutical delivery. Crosslinking of starch molecules reinforces the hydrogen bonds present in the starch granules with the new and more stable covalent bonds (Acquarone & Rao, 2003). Resulting in tight packing of molecules resulting from their inter-molecular bridging. The larger the number of hydrophilic groups in the polymer chain; the higher will be their water absorption capacity (WAC). However, the degree of crosslinking was found to be inversely related to its viscosity and swelling power. This is because higher crosslinking leads to a smaller granule volume (Shah et al., 2016). There was a higher crosslinking in amino acid modified starch since the acidic nature of amino acids directs more hydrogen ions to the starch chains, probably reducing the negative charge of the phosphate groups of the starch granules, increasing the attraction among the molecules thus facilitating higher crosslinking, subsequently reducing the PV. This crosslinking results in a higher degree of interaction among the starch chains than between the starch and water, decreasing the WAC, swelling, viscosity, producing a weaker gel with higher adhesiveness.

Srichuwong et al. (2017) studied the effects of starch and non-starch components on physicochemical properties and starch digestibility of millets. Here starch hydrolysis was increased by the removal of surface proteins by pepsin. Studies also suggest that the hydrolysis of protein matrix by proteases could release the phytic acid and phenolic compounds from the grain matrix, inhibiting the α-amylase and reducing the rate of starch digestion in the GIT (Deshpande & Cheryan, 1984). Shape, size, surface-to-weight ratio and processing also influence the nutrient bioavailability as it determines the accessibility of a nutrient from the

food matrix. A higher drying temperature was shown to reduce the in vitro starch and protein digestibility in cereal-based food matrices (Petitot, Brossard, et al., 2009). This could be due to increased intermolecular cross-linking of proteins causing their stable aggregates which are resistant to digestion under elevated temperature. These aggregates also encase the starch, reducing its susceptibility to digestive enzymes (Stuknytė et al., 2014). The susceptibility of gelatinized starch to disintegration or fragmentation indicates its cooking or breakdown stability. Higher breakdown values suggest the reduced capacity of the flour to resist mechanical stress and heating conditions during cooking. Millet flours display a lower breakdown (1.12 to 29.49%) when compared to that of wheat flour (35.91%). This was due to the adsorption of protein molecules on the exterior surface of the cooked starch molecules, preventing the breakdown under shear stress (Fig. 2C) (Derycke et al., 2005).

4.1.3. Lipid-Protein interaction

Lipids and proteins, either as complex or independently have important functional roles in food. The structural configuration of protein-lipid complexes in the biological system is dissimilar from those formed during food processing. Regardless, the physicochemical properties of these complexes during food processing resulting from mixing, storage and heating are very similar to those of protein-lipid complexes found in the living system. Chemical bonding involved in protein-lipid interactions includes covalent bonding, hydrophobic interactions, van der Waal forces, and electrostatic interactions. For a given lipid and protein system, the interactions may differ depending on the temperature, pH and ionic strength of the medium. For example, at acidic pH, proteins carry a positive charge which can bind the negatively charged phospholipids and at basic pH, proteins exhibit negative charge resulting in electrostatic repulsion and a decreased propensity to interact. Also, more than one type of bond may be involved in these interactions. Electrostatic interactions could take place between a positively charged protein group (guanidyl or lysyl or amyl) and a negatively charged phosphate group of phospholipids. Also, between a negatively charged protein group (glutamyl, aspartyl) and positively charged choline of phospholipid.

Additionally, several dipole interactions occur between uncharged polar molecules where electrons are spread in such a way that there is a surplus of positive charge in one region and an excess of negative charge in another. These electrostatic forces between polar lipids and polar amino acids are involved in bread and dough making. Proteins react with oxidized lipids, forming covalent bonds imparting more functional and structural stability to lipoproteins in both food products. Lipids also interact with proteins by forming hydrogen bonds between the fatty acid hydroxyl group, di or monoglyceride, phospholipid head groups (phosphatidylserine) and the protein carbonyl groups (Alzagtat & Alli, 2002). Earlier the protein-lipid interaction was said to involve electrostatic interactions but was later proven to interact by hydrophobic bonds (Gentile, 2020). Hydrophobic interactions are entropy-driven and endothermic with their strength increasing with temperature. These hydrophobic interactions between lipids and proteins can modify the protein structure by reducing their intramolecular hydrophobic bonds, causing the partial unfolding of the protein structure at the oil–water interface. Proteins unfold to expose their reactive amino acids, which have the potential to form disulfide and hydrophobic interactions with the molecules in their proximity, giving rise to an immensely viscoelastic membrane. These hydrophobic interactions govern protein aggregation and are important factors for determining the protein-lipid interactions. For example, making good quality bread from wheat involves hydrophobic bonds between lipids and glutenin and hydrophilic bonds between gliadin and lipids. Protein lipid complex is also stabilized by short-range non-specific van der Waals forces caused by interactions among adjacent molecules or atoms and induced dipoles, and thus concerned to the polarizability of molecules or atoms. These are extremely weak interactions individually but have the potential to

stabilize the protein-lipid complex collectively. The CH_2 groups of fatty acids can attract the CH_2 groups of protein side chains, to stabilize the protein-lipid complex.

4.1.4. Binary interactions with phenols

Polyphenols are a major group of plant secondary metabolites, intensively explored due to their potential positive effects on human healthcare. Their bioavailability and mechanism of action have been widely studied, both in vivo and in vitro (Kumar et al., 2020). Recently numerous studies indicate the intricate interactions between phenols and food matrix components like lipids, proteins and carbohydrates, significantly affecting the phenolic compound activity. Polyphenols display a large diversity in their bioactivities in human metabolism and nutrition by modulating numerous vital metabolic pathways (Hollman et al., 2011) and interaction with food matrix components (Bourvellec & Renard, 2012). The bioavailability and bioaccessibility of polyphenols do not directly correspond to their comparative abundance in the food matrix. The structural integrity of plant material where they are integrated along with their chemical interactions with diverse food components is critical for their proper release and their subsequent intake into the living system through the intestinal epithelium (Raikos, 2017). Cooking significantly influence the bioavailability of polyphenols like carotene, as its release in the GIT is directly related to the deterioration of the matrix organization. A study was conducted to understand the effect of parboiling on the availability of phenolics in millet porridge and couscous. They indicated an increase in the total free phenolic content of pearl millet porridge and couscous made from parboiled grains when compared to those prepared from non-parboiled grains (Bora et al., 2019). This could be due to the restricted migration of phenolics from the pericarp to the inner grain layers and the subsequent release of bound phenolics from the matrices during the parboiling process (Paiva et al., 2016).

Polyphenols interact with lipids from the food matrix and reduce fat absorption, influencing health (Uchiyama et al., 2011). After ingestion, the dietary fats are masticated into emulsions. Lipases break the lipids into smaller components and enable their intestinal absorption. Certain emulsion characteristics like surface area and droplet size determine the lipase activity and extent of lipid breakdown (Shishikura et al., 2006). Polar molecules are found in the aqueous phase, non-polar molecules in the lipid phase and amphiphilic molecules at the interface between these two phases. These molecules can alter the size or surface area of the oil droplet and are important determinants of lipase activity. Polyphenols can affect the emulsions by decreasing their surface area and increasing the droplet size. For example, hydrophilic heads of phosphatidylcholine at the surface of the emulsion droplet interacts with hydroxyl groups of surrounding polyphenols to form complexes. The interaction of these complexes is further assisted by phenols to form aggregates, increasing the droplet size. Their large droplets decrease lipase activity and fat absorption. These polyphenols can also directly inhibit lipase activity (Fig. 1G). Lipids in the food matrix can also capture these polyphenols and shield them against degradation during their gastrointestinal tract passage. Thus, assisting the polyphenol delivery, stability and action in the lower portions of the gastrointestinal tract. These polyphenols primarily generate an antioxidant environment and counter harmful lipid peroxidation products like malondialdehyde. They also influence the millet starch pasting profile by competing with starch for binding with water molecules, reducing the water content in the system (Sharma & Gujral, 2019b; K. Wu et al., 2016).

Various non-covalent forces like hydrogen bonds, hydrophobic, and electrostatic interactions have been known to determine the starch (both raw and gelatinized starch) and polyphenol interaction in millets (Sun et al., 2016; Zou et al., 2016). Interactions between phenolic compounds and starch greatly influence the nutritional attributes, physicochemical, and/or technofunctional properties like retrogradation, gelatinization, rheology, and digestibility of millet based foods (Li et al., 2020; Vinutha et al., 2022). On a molecular level, the interaction between various

starches and polyphenols could form two types of complexes. One is the V-type inclusion complex where the phenolic compounds are partially enclosed within the inner hydrophobic starch helix (Luo et al., 2020). The other is the non-inclusion complex where the carbonyl and hydroxyl groups of the phenolic compounds interact with starch forming intermolecular aggregates (Deng et al., 2021; Zhu, 2015).

Interactions between starch and phenolic non-inclusion complexes are based on electrostatic and hydrophobic interactions, while hydrogen bonds are the predominant binding forces. A model of non-inclusion complex where numerous polyphenol molecules circumscribe multiple starch helices via hydrogen bonds and two to three weak CH-π bonds was given by (Fig. 3E, F, G) (Guo et al., 2019). Phenols can also suppress the breakdown of hot millet starch paste. Millet flours also display a lower retrogradation rate (17.73 to 31.88%) as compared to the higher retrogradation rate of wheat flour (34.80%). Low retrogradation rate millet flour could result from the behaviour and nature of starch and higher phenolic content (Wu et al., 2009). Retrograded starch contains stable hydrogen bonds in its structure, forming a cement structure with amorphous regions. The interactions between phenols and retrograded starch are chiefly governed by the hydrogen bridges made by hydroxyl groups. Since phenols contain numerous reactive OH groups, they can interact with retrograded starch by strong hydrogen bonds. These interactions strongly impede the realignment and reassociation of starch polymeric chains in retrograded starch, preventing their recrystallization (Sharma et al., 2017). Also, the high reactivity of OH groups increases their potential to compete and form stable hydrogen bonds with starch. Millet phenolics were also studied for their α-glucosidase and α-amylase inhibitory activities (Pradeep & Sreerama, 2015). The inhibition of these enzymes showed anti-diabetic effects by amelioration of postprandial glycemic response. Studies indicate that these phenolic compounds interact with reactive amino acid side chains in the active site of the enzymes. This alters the physicochemical properties of the enzymes like electrophoretic behaviour, solubility, secondary and tertiary structure, molecular weight, hydrophobicity, and thermodynamic parameters (Aleixandre et al., 2022). Polyphenols also bind millet starch by inhabiting the hydrophobic helical areas of starch, interrupting the α-amylase action (Andrade et al., 2022). The digestibility, structure, pasting, and swelling power of proso millet starch with different proanthocyanidin concentrations were assessed (Xiao et al., 2021). The results indicated that swelling power and solubility of proso millet starch increased with an increase in proanthocyanidin content. The pasting profile indicated that the addition of proanthocyanidins to the millet matrix increased the peak viscosity while decreasing the setback and pasting temperature. The authors stated that the phenolic hydroxyl groups of proanthocyanidins may interact with starch hydroxyl groups increasing swelling power and solubility, loosening the starch structure.

Starch obtained from the millet based foods is primarily digested in the small intestine. After starch digestion, the final product glucose present in the intestinal lumen is transported through the enterocytes into the blood by glucose transporters, like glucose transporter 2 (GLUT2), sodium-coupled glucose transporter 1 (SGLT1), etc. This increases the postprandial blood glucose level, delivering it to tissues like muscle and liver cells (Pan et al., 2022; Sun & Miao, 2020). The effect of dietary polyphenols on glucose transport in cells is frequently studied using tissue cancer cell models. Polyphenols have been shown in most investigations to reduce glucose uptake by intestinal cells (Caco-2 cells) via inhibiting glucose transporters such as SGLT1 and GLUT2 (Mieres-Castro et al., 2022). Furthermore, dietary polyphenols have been shown to suppress the expression of SGLT1 and GLUT2 in the intestine. Inhibiting glucose transport into intestinal cells helps to keep blood sugar levels under control. Due to the accumulating effect of the final catalytic product of starch digestion, glucose in the colon is also suggested to delay the enzymatic reaction (Fig. 4) (Wu et al., 2022). Dietary polyphenols, on the other hand, have been proven to have the opposite
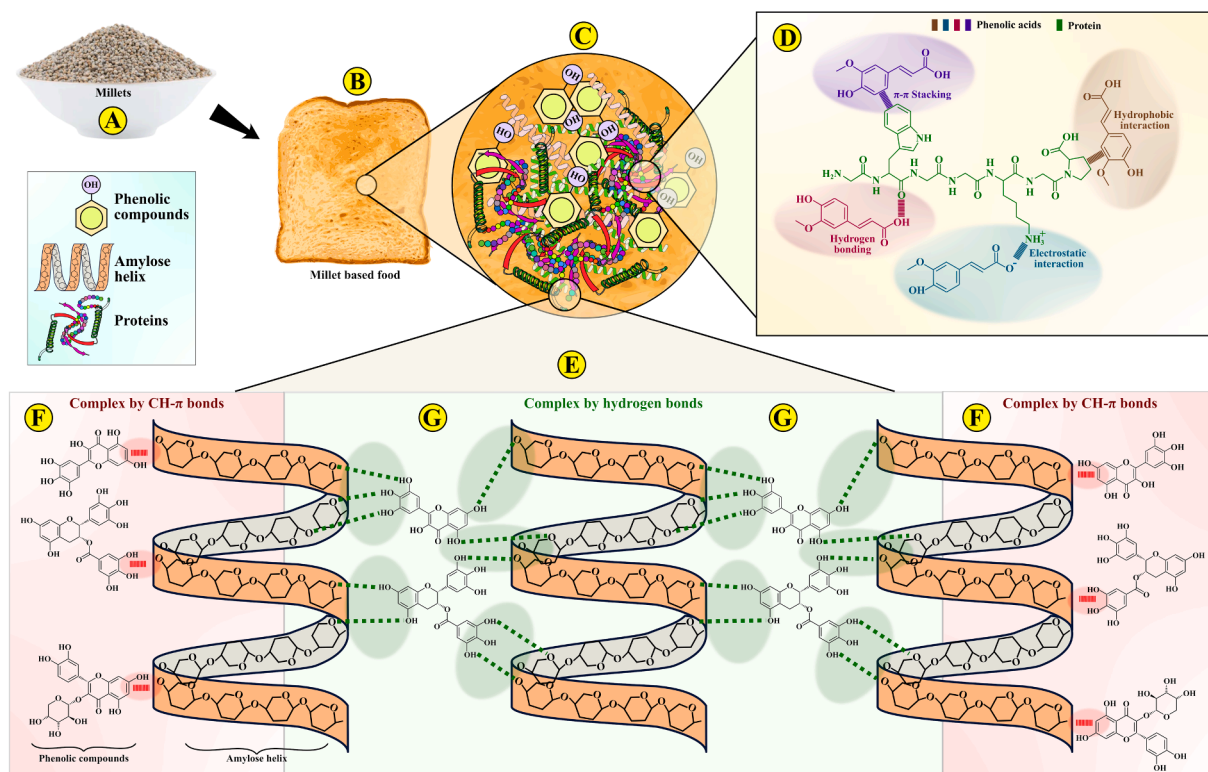
Fig. 3. Shows varous phenol-starch and phenol–protein interactions. A) Millet grains; B) Millet based food (bread); C) Millet based food matrix containing starch, proteins, and phenols; D) Various types of interactions between protein-phenols like π-π stacking, hydrophobic interactions, electrostatic interactions and hydrogen bonds represented through different colours; E) Non-inclusive complexes interactions between starch and phenols; F) Interaction between phenols and starch by CH-π bonds; G) Interaction between phenols and starch by hydrogen bonds.
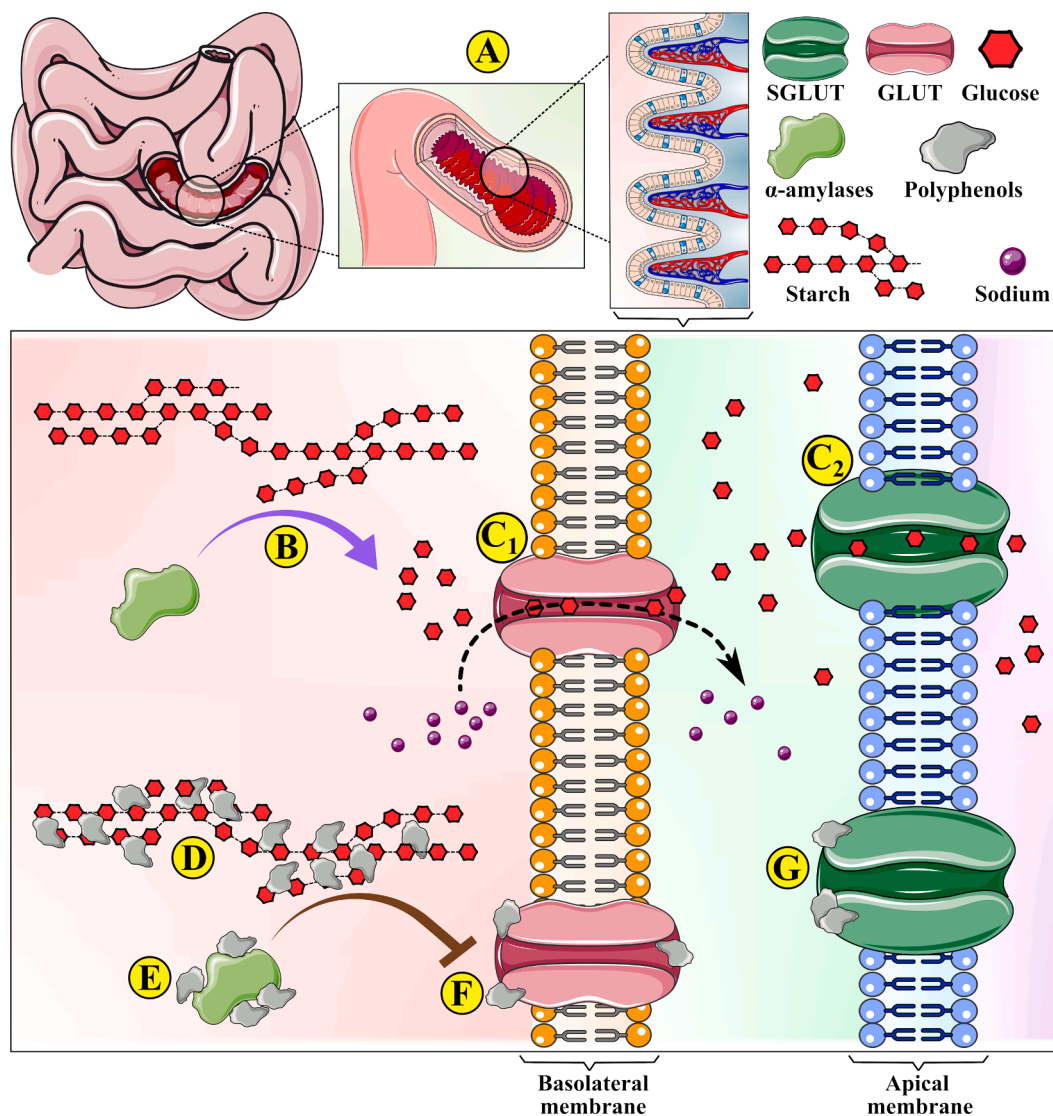
Fig. 4. Control of blood glucose levels by phenol interactions in millet based foods. A) Intestinal lumen of the the small intestine; B) Hydrolysis of millet starch into glucose by hydrolytic enzymes like α-amylase; C) Transport of glucose across the (C_1) basolateral membrane by sodium-coupled glucose transporter (SGLUT) and (C_2) apical membrane by glucose transporter (GLUT) transporters; D) Binding of polyphenols to the starch molecules; E) Binding of polyphenols to the starch hydrolyzing enzymes like α-amylase, inhibiting their catalytic action; F) Inhibition of glucose transport across the basolateral membrane by polyphenol binding to SGLUT; G) Inhibition of glucose transport across the apical membrane by polyphenol binding to GLUT.

effect on other cellular systems. Resveratrol and ergosterol, for example, have been shown to stimulate GLUT4 expression and thereby boost glucose transfer into muscle cells (Xiong et al., 2018). Furthermore, it has been found that protopanaxadiol and epigallocatechin-3-gallate enhance glucose transport into liver cells (HepG2 cells). Stimulating glucose transport into these tissue cells could also further aid in blood sugar reduction.

During the processing of millet based foods, the proteins show a tendency to form higher molecular weight aggregates and networks. Here the protein's structure and the accessibility of certain amino acid side chains for matrix interactions are pivotal. A multitude of distinct characteristics influences the interactions between proteins and phenolic acids. In addition to the parameters that directly influence protein structure ('denaturation'), such as pH, salt, temperature, and protein concentration, the phenolic acid structure greatly influences the type of interactions (Sęczyk et al., 2019). The properties of phenolic acids determining the non-covalent interactions include the benzene ring, double bonds (in the side chains), partition coefficients (log *p* values), and keto-groups (Nagy et al., 2012). Non-covalent interactions

between proteins and phenolic acids in millet based food matrix are generally reversible. These can take place via different types of mechanisms: π-bonding/π-π-stacking, van der Waals interactions, hydrophobic interactions, electrostatic interactions, and hydrogen bonding (Fig. 3C, D) (Guan et al., 2021). These interactions are highly unstable and are determined by temperature, ionic strength and pH. A low to neutral pH favours the formation of non-covalent bonds, while the ionic strength influences the electrostatic interactions, which in turn are influenced by the protein's isoelectric point (Günal-Köroğlu et al., 2022). The temperature chiefly governs the formation of hydrogen bonds and hydrophobic interactions. Higher temperature increases the magnitude of hydrophilic interactions, while extreme temperatures can break these interactions.

Phenols can also irreversibly associate with proteins by covalent bonds, where phenols are converted to quinones and subsequently react with nucleophilic protein groups. Polyphenols with high molecular weight (tannins) display a strong binding capacity with proteins (Jones-Moore et al., 2022). Polyphenols with high structural flexibility bind more readily to some proteins (bovine serum albumin and gelatin),

while those with less flexibility (ellagitannins) interacts strongly with some proteins (gelatin) and weakly binds with others (bovine serum albumin). Also, the potential of polyphenols to bind proteins directly relies on their OH groups. Since the millet based food matrices have a diverse amino acid composition, phenolic acids bind to the hydrophobic pockets in a protein, changing protein folding, structure, and functionality (Guan et al., 2021). The hydrophobic interactions between phenolic acids and proteins take place at domains/ regions of protein where a high number of amino acid residues like valine, isoleucine, leucine, phenylalanine, proline, methionine, glycine, cysteine, and alanine are present. Side chains of tryptophan, tyrosine, threonine, serine, glutamic acid, glutamine, histidine, lysine, cysteine, aspartic acid, arginine, and asparagine have a higher propensity to interact through hydrogen bonds (Yu & Liang, 2021). This can further block several essential amino acids, influencing their bioavailability.

The effect of phenol–protein interaction on protein digestibility was analyzed on millet-based products (couscous and porridge) (Bora et al., 2019). These interactions decreased the protein digestibility of couscous and porridge from 52.0% to 44.6% and 52.7% to 44.3%, respectively which can be explained based on the complex formation between the hydroxyl groups of phenolic acids and amino acid side chains of specific proteins. Phenolic acids can also oxidize to generate peroxides, which can consequently oxidize the amino acids, causing protein polymerization, reducing the overall protein digestibility (Duodu et al., 2003). Similarly, finger millet flour was composted with cowpea and the sensory properties and anti-nutritional contents in contemporary porridge made by them were determined (Syeunda et al., 2019). Here the protein digestibility decreased because the condensed tannins in millets formed an indigestible tannin-protein complex, via hydrogen bonding and hydrophobic interactions. The prolamins in finger millet (eleusinin) are proline-rich and thus strongly bind to tannins and phenols, reducing their digestibility (Anyango et al., 2011a). Also, the condensed tannins break to form flavanols, which can exercise certain stearic effects on protein structure, altering their quality.

Polyphenol–protein interactions also affect the astringency sensation (rough, puckering, and drying mouth-feel) (Fig. 2G) (Perez-Gregorio et al., 2014). This reduces the lubrication of saliva, causing an unpleasant sensation. A substantial difference in the astringency aftertaste between malted and unmalted millet porridge was observed (Syeunda et al., 2019). The unmalted millet porridge showed a higher astringency due to its high content of polyphenols and tannins. The malting reduces the tannin and polyphenol content, explaining the lower astringency in malted millet porridge. Phenols also interact with carbohydrates by the formation of hydrogen bonds between the oxygen atoms of glycosidic linkages and hydroxyl groups of polyphenols. These interactions also regulate the bioavailability of phenolic compounds and carbohydrates. A study demonstrated the highest RDS, which could be due to the higher phenolic content that inhibits the enzyme hydrolysis by adsorption on the surface, decreasing the starch digestibility (Sharma & Gujral, 2019b).

4.1.5. Mineral interactions

Millets are known for their rich micronutrient content; their mineral bioavailability is also a vital trait influenced by other food matrix components. They are either intrinsically present in the food or added at the time of cooking or processing. Minerals exist as free ions, complexes, and compounds in the food matrices. Their free ionic forms are highly reactive due to their high solubility and their tendency to quickly interact with food matrix components by coordination bonds, covalent, electrostatic and so on. Also, the presence of absorption inhibitors in the matrix, in turn, affect mineral bioavailability. Polyphenols and phytates are two prevailing compounds present in cereal-based food matrices. These inhibitory compounds form complexes by strongly chelating macro (Calcium) and micro (Iron and Zinc) nutrients and notably reduce their uptake from the food matrix resulting in malnutrition in vegetarians. Also, humans cannot hydrolyze phytates in their GIT causing a mineral deficiency (Fig. 1F).

In a study, pearl millet porridge was fortified by baobab fruit, moringa leaves, citric and ascorbic acid and was analyzed for mineral bio-accessibility (Adetola et al., 2019). Total bioaccessible and percentage bioaccessible iron increased in millet + citric acid and millet + baobab by 52% and 30%, and by 52% and 36%, respectively compared to millets alone. Also, the incorporation of citric acid enhanced zinc bio-accessibility. This could be because citric acid and ascorbic acid from baobab fruit are known as effective enhancers of mineral bioavailability in foods. They effectively chelate minerals and maintain them in an absorbable and soluble form (Iyengar et al., 2010). Ascorbic acid also acts as a reducing agent for an apical membrane-bound ferrireductase. This enzyme reduces Fe^{3+} to Fe^{2+}, which is the only conformation in which non-haem iron can be transported through the intestinal membrane (Mackenzie & Garrick, 2005). Contrastingly, millet + moringa lowered the bioaccessibility of zinc and iron. This could be due to the presence of a high concentration of antinutritional factors like phytates, tannins and calcium. Calcium forms strong insoluble complexes with zinc and phytates, reducing their bioavailability. Some phenolics also reduce the zinc uptake by the intestinal cells. The content of mineral binding phenolics also varies due to their tendency to bind organic compounds like proteins, also a change in these protein structures could reduce the mineral sequestering properties of phenolics (Pandey & Rizvi, 2009).

Finger millet and sesame fortified breads were evaluated for mineral bio-accessibility (Agrahar-Murugkar, 2020). These breads showed high calcium and zinc bio-accessibility. The authors stated that the protein content in the food matrix, enhances the bioavailability of various minerals, presumably by forming amino acid complexes, facilitating their absorption (Sandström et al., 1980). Porridges were prepared from whole grain pearl millet, blended with carrot (provitamin A), *Moringa oleifera* leaf and *Adansonia digitata* (Baobab) powders. There was an apparent increase in the stability and bioaccessibility of provitamin A carotenoids from these blends. The authors indicate that the use of Baobab could enhance the micellization (bioaccessibility) and digestive release in the GIT. Baobab contains a high amount of citric and ascorbic acid which assists the stabilization of carotenoids in micelles, while iron precipitates fatty acids and bile salts and reduces the formation of β-carotene micelles (Ndiaye et al., 2020).

The texture quality of gels made from foxtail millet flour at different concentrations (ranging from 9 to 13 %) along with selected cations and hydrocolloids, were determined. Various concentrations of divalent ($FeSO_4$ and $CaCl_2$), monovalent (NaCl) cations, and hydrocolloids like agar, xanthan, starch, gellan, and gelatin were incorporated in the gels (Nagaprabha & Bhattacharya, 2016). The gel forming ability significantly improved with the increase in the concentration of $FeSO_4$ and $CaCl_2$, while NaCl showed a marginal effect. The authors stated that these salts stimulate the solubilization of salt soluble proteins in a way that these proteins form a part of the sol and participate in the gelling process.

Agte et al. (1999) conducted a study to investigate the nutritional bioavailability of iron and zinc in sorghum and pearl millet using weanling mice as a model for in vivo analysis. The results indicated a higher absorption and activities of these trace minerals, which could be attributed to a lower ratio of phytate to iron and zinc. Similarly, the role of mineral inhibitors like condensed tannins, phenolic compounds and phytic acid was studied on zinc and iron sour porridge made by finger millet (Gabaza et al., 2018). It is widely known that these inhibitors significantly reduce mineral bioavailability by sequestering them. The process of fermentation inactivates the phytates by breaking them into lower inositol phosphates, which have a low potential for mineral binding. Also, the enzymes like glucosidases, esterases, reductases and decarboxylases chemically transform the condensed tannins and phenolic compounds, reducing their inhibitory effects (Svensson et al., 2010).

4.1.6. Ternary interactions

Three-component interaction between lipids, proteins and starch affects the functional and nutritional quality of foods (Zhang et al., 2006). Ternary interaction between lipid, protein and starch has been extensively studied by rapid visco analyser (RVA) (Fig. 2A) and high-pressure size exclusion chromatography (HPSEC) (Zhang et al., 2003; Zhang & Hamaker, 2003). During RVA cooling (setback) the amylose and amylopectin chains realign to form a highly crystalline matrix. A higher setback viscosity during cooling indicates a higher propensity of amylose to retrograde while lower setback viscosities suggest a reduced retrogradation tendency. A system containing whey proteins, fatty acids (linoleic or oleic acid, palmitic acid) and sorghum starch exhibited a distinct viscosity peak at the time of setback (RVA cooling) and a peak during HPSEC was eluted between the amylopectin and amylose peaks. These observations were ascribed to the generation of protein-lipid-amylose complexes (Zhang et al., 2003; Zhang & Hamaker, 2003). Integration of β-lactoglobulin (protein) with a mixture of starch and medium-chain fatty acids (decanoic and lauric acid), enhance the intensity of setback peak when compared to that of the fatty acid–starch mixture (Zheng et al., 2018). These findings further confirm the formation of a ternary complex between protein, starch, and fatty acids during cooling-heating cycles. XRD and DSC studies on ternary complex signify that the fatty acids interact with amylose through their aliphatic tails, whereas the negatively charged carboxyl fatty acid groups engage with the protein structure. Since amylose is a neutral molecule, it does not contribute to ionic interactions (Zheng et al., 2018). Structural analysis of the ternary complex (starch-fatty acids-proteins) indicates that they have a larger long- and short-range structural order than the corresponding binary interactions (starch-fatty acids).

Several studies have confirmed the formation of the ternary complex using different starch-lipid-protein mixtures (Wang et al., 2017; Zheng et al., 2018). A study was focused to investigate the mechanism of interactions between native starches, proteins and lipids in foxtail millet and their effect on in vitro starch hydrolysis (Jin et al., 2019). They established that protein matrix not only functions as a physical barrier between starch and starch digesting enzymes (α- amylase) but also moderately sequesters α-amylase, arresting the starch hydrolysis in foxtail millet flour. Integration of foxtail millet starches with FFA (free fatty acids) can further reduce the starch hydrolysis rate.

Annor et al. (2013) studied the effect of protein-lipid-starch interaction on the expected glycemic index (eGI) and in vitro starch digestibility of kodo millet flour. The dense millet flour matrix containing components like minerals, phenolics, lipids, proteins, and fibre cause macromolecular crowding or inhibition or masking of the hydrolytic enzymes affecting starch hydrolysis (Krishnan, Awana, et al., 2021; Krishnan, Mondal, et al., 2021; Krishnan, Rani, et al., 2021). A substantial increase in the eGI and in vitro starch digestibility was observed after removing proteins (protease treatment), fats (defatting) or both, with lipids demonstrating a larger impact than that for proteins. Proteins create a stable barrier, encapsulating and entrapping the starch granules by creating a continuous matrix, preventing the accessibility of starch hydrolyzing enzymes. Lipids also restrict enzyme-mediated starch degradation by forming a resistant complex between lipids and amylose. Cooking these samples increases the hydrolysis caused by starch gelatinization, increasing its accessibility for amylolysis. XRD and DSC on ternary complex revealed that the aliphatic FA tail interacts with amylose, and the negatively charged FA carboxyl group coalesces with protein, while amylose being a neutral molecule do not impart ionic interactions (Wang et al., 2017).

Traditional food called 'Rabadi' is made from the fermentation of pearl millet with the addition of buttermilk made from defatted cow or buffalo milk yoghurt. This food was modified by replacing the buttermilk with camel milk and adding soybean and fruit pods of (*Prosopis cineraria*) and analyzed for their protein, starch, and nutrient bioavailabilities (Saraswat et al., 2020). The addition of camel milk increased the protein digestibility of the food, which could be due to less fat content in camel milk. The higher fat content of buffalo or cow milk induced stable emulsification with proteins, decreasing their bioavailability. Also, the phenols of *Prosopis* pod precipitates the proline-rich protein fractions, increasing their bioavailability (Keogh et al., 2007). The presence of more fatty acids also reduces the starch hydrolysis, due to the formation of the starch-lipid complex (Annor et al., 2015).

Another study was aimed to ascertain the effect of finger millet flour on drinkable cassava porridge with respect to starch digestibility, nutrient bioavailability, sensory attributes, and physicochemical properties governed by interactions between protein, starch and lipids (Onyango et al., 2020). Millet flours showed delayed gelatinization due to the competition between fibre and starch for water molecules, while lipids restrict starch swelling by forming a complex with amylose. Also, the slurry made by finger millet flour showed a low viscosity due to the hydrogen bond formation between the starch hydroxyl groups and proteins, impeding the starch retrogradation (Anyango et al., 2011b). α-amylase mediated starch hydrolysis decreases the water holding capacity of the starch in millet flour integrated cassava porridge, enabling to double the amount of flour without altering the drinkable consistency of porridge.

Whole grain breads were prepared using blends of raw and extruded flours from millet and their physicochemical parameters were evaluated in comparison to commercial whole bread products with and without gluten (Pessanha et al., 2021). The bread products showed lower *In vitro* antihyperglycemic properties which could result from starch-lipid-phenol interactions. The authors stated that starch digestibility is modulated by two main mechanisms, namely, modulating the glycolytic enzymes and/or the formation of supramolecular complexes between phenolic compounds, starch and/or lipids. Presumably, one mechanism cannot exclude the other, but it could play a complementary role in modulating starch digestion (Giuberti et al., 2020).

4.1.7. Other interactions

Several technical challenges exist in replacing wheat flour with millet flour since they deteriorate the bread quality with respect to staling rate, mouth-feel, texture and loaf volume (Aprodu & Banu, 2015). Gluten protein interactions are important for making a solid matrix network, permitting gas retention, improving bread volume, maintaining bread softness, and reducing stalling. Replacement of glutens with hydrocolloids like dextran can be used to prepare high-quality bread. Dextrans are α-glucan polysaccharides synthesized by lactic acid bacteria. A study was conducted to investigate the interactions between dextrans and other food matrix components in pearl millet bread, and their influence on its nutritional, technological, and rheological characteristics (Wang et al., 2019). Dextran (3.5%) enhanced the extensional properties of whole-grain pearl millet bread containing gluten, by raising the bread specific volume, reducing crumb firmness, staling rate, and moisture loss. The positive implications of dextrans on millet dough rheology are related to their molecular conformation, chemical structure and concentration which ascertains their intermolecular interactions with dough matrix components. Dextrans interact with gluten proteins in the millet bread matrix by steric interactions or/and hydrogen bonding, acting as an additional supporting framework for the gluten network and strengthening the dough structure. This structure increases the dough film stability around the expanding gas cells, reducing the gas diffusion, foam collapse, increasing the loaf volume (Zannini et al., 2014). Also, interactions between dextrans and starch, reduces the retrogradation enthalpy and amylopectin crystal reformation, lowering the staling rate. Dextrans can also interact with millet protein and starch, decreasing the starch-protein and starch-starch, accelerating the bread hardening (Fadda et al., 2014).

Studies indicate that the DFs in the millet based food matrix have a trifling effect on eGI (Mitharwal et al., 2021). A study was conducted to assess the nutrient digestibility and physiochemical properties of DF fortified millet breads also showed a similar effect (Li et al., 2020). The authors observed that the addition of ~ 5% DF or millet flour did not

Table 1
Interactions between various components in millet based food matrices.

Matrix interaction	Interacting matrix components	Millet	Important findings	Reference
Binary	Starch and lipid	PM, FiM, PrM, FoM	• Significant reduction of in vitro hydrolysis of the starches and eGI • The reductions in *in vitro* starch hydrolysis of the millet starches relied on the amount of fatty acid added • The starch-fatty acid complex decreased the starch hydrolysis in the following order; oleic acid > linoleic acid > palmitic acid • The reduction in starch hydrolysis was less in pearl and finger millet starches than in proso and foxtail millets • The RS content increased while the RDS decreased with the addition of fatty acids to all millet starches	(Annor et al., 2015)
Binary	Starch and lipid	PM	• *In-vitro* oro-gastro intestinal simulation revealed pearl millet to have lower IGP of 63.71%, when compared to that of rice (65.89%) • High density of food matrix components and higher starch-lipid interaction visualized by CLSM contributes to the resistance towards starch hydrolytic enzymes • The long hydrophobic lipid tail enters the cavity like structure of amylose facilitates starch to form a stable complex, thereby impeding the accessibility of starch to hydrolytic enzymes	(Mondal et al., 2022)
Binary	Starch and lipid	FoM	• The dissociation temperature of ALC is increased with an increase in the length of the lipid hydrocarbon chains and decreased with an increase in the number of double bonds in the lipid hydrocarbon chains • The amylose–PA complexes showed the highest dissociation temperature when compared to the amylose complex with OA and LA • When the millet starch was incubated with hydrolytic enzymes, the % hydrolysis of starch alone (control) was 84% and was subsequently reduced to 71.1% after cooking with OA, followed by LA (75.0%) and PA (76.9%) • The formation of an ALC also inhibits the swelling of starch granules, further reducing the starch hydrolysis	(Jin et al., 2019)
Binary	Protein and starch	FoM	• At 120 min of starch hydrolysis, 50.4% of starch was hydrolyzed in the case of pepsin-treated millet flour (deproteinated), compared to 42.5% for undigested (proteinated) millet flour. • Proteins formed a physical barrier between starch and degrading enzymes by forming a starch-protein matrix and subsequently encapsulating the starch	(Jin et al., 2019)
Binary	Protein and starch	PrM	• The addition of zein, SPI and WPI decreased the RDS to 8.4% and 14.6% respectively and increased the RS to 17.5% • The FV and SB of the starch–protein mixtures were lower than those of the millet starch, while the BD was higher • The addition of zein increased the TV and PV, while decreasing the PT when compared with millet starch • The addition of WPI and SPI resulted in a decrease in PV • The SB values depicting the retrogradation and stability of starch cold paste of all starch–protein mixtures were less than those of the millet starch	(Zheng et al., 2020)
Binary	Protein and starch	KuM	• Millet starch modified with lys, thr and asp were characterized for their various functional, structural, pasting, and textural properties • Lys was found to be a better cross linker for millet starch modification and preparation of their gels for nutraceutical delivery • The amino acid modified millet starch showed a higher DC (11.05–35.71%) • Millet starch modified with the amino acid at a higher pH showed good textural properties when compared to those at lower a pH • The amino acid mediated crosslinking in the millet starch decreases the WAC, swelling, viscosity, producing a weaker gel with higher adhesiveness • Lys-modified millet starch showed the highest SP (12.34 g/g) at pH 9, which might be due to its lower DC	(Mahajan et al., 2021)
Binary	Protein and starch/ Starch-fibre	PM	• Proteins delayed starch gelatinization and pasting • TDF retarded starch retrogradation • Enzymatic hydrolysis of starch was impeded by the presence of associated protein matrix	(Srichuwong et al., 2017)
Binary	Starch and phenols/ protein and phenols	PM, PrM	• Parboiled PM and PrM showed a 37% and 28% increase in decortication yield, respectively, when compared to non parboiled samples • Decortication significantly altered the starch digestion fractions thereby reducing eGI while the IVPD of products decreased by 14–17% • Parboiling decreased IVPD of PMPo, PMCo, PrMPo and PrMCo by 17%, 15%, 14% and 16%, respectively due to complex formation between the hydroxyl groups of phenolic acids	(Bora et al., 2019)
Binary	Starch and phenols	PrM	• Polyphenols (proanthocyanidins) increases the solubility and swelling power of starch from 5.32% and 13.77 g/g to 16.35% and 19.83 g/g, respectively • Polyphenols increased the PV of starch (from 2284.5 cP to 2335 cP) while reducing the PT and SB (from 372.5 cP to 297 cP) • A significant decrease in enthalpy was measured by DSC, the enthalpy decreased from 14.98 J/g to 10.24 J/g at a 20% proanthocyanidin concentration • Proanthocyanidins reduced the RDS and increased the RS content (from 71.31% to 74.55%)	(Xiao et al., 2021)
Binary	Starch and phenols	FiM	• The protein digestibility decreased because the condensed tannins in FiM formed an indigestible tannin-protein complex, via hydrogen bonding and hydrophobic interactions.	(Syeunda et al., 2019)

(continued on next page)

Table 1 (*continued*)

Matrix interaction	Interacting matrix components	Millet	Important findings	Reference
Binary	DF-starch	PM	• Steamed MF (25%) and DF significantly affected the dough farinographical and tensile properties • MF with 2% DF showed good sensory performance and medium GI • DF in MF gradually decreased the RDS and SDS and increased the RS	(Li et al., 2020)
Binary	Protein-mineral	FoM	• FoM gels showed improved gel forming ability with the increase in the concentration of FeSO$_4$ and CaCl$_2$ due to the solubilization of salt soluble proteins in a way that these proteins form a part of the sol and participate in the gelling process	(Nagaprabha & Bhattacharya, 2016)
Ternary	Starch-protein-fibre	FiM, FoM, KM, LM and PrM	• Significant improvement in DDT, stability, protein weakening, gelatinization temperature and reduction in peak viscosity, starch gelatinization rate and retrogradation of MFs supplemented with 12% exogenous vital gluten protein • WAC of the dough significantly enhanced and was positively correlated with arabinoxylan and dietary fibre content • The positive role of arabinoxylan, TDF and exogenous vital gluten in lowering starch retrogradation • The flour blends displayed up to 49.73% higher SDS, 81.63% more RS, up to 41.49% less RDS and 11.55% lower pGI	(Sharma & Gujral, 2019a)
Ternary	Starch-lipid-phenol	PM	• Whole PM grain bread products showed lower In vitro antihyperglycemic properties which could result from starch-lipid-phenol interactions • The anti-hyperglycemic activity of breads prepared from raw whole grain PM flour (90.3%) and precooked PM flour (99.2%) were 20–30% higher than the hypoglycemic drug	(Pessanha et al., 2021)
Other interactions	Starch-protein-phenols-fibre	FiM, FoM, KM, LM and PrM	• Total arabinoxylan and TDF content significantly increased protein weakening • PV was negatively correlated with phenolic content • Phenolics and TDF and suppressed retrogradation • IVPD was negatively correlated with tannin, phytic acid, phenolics, flavonoids and TDF content • RS was positively correlated with TDF, phenolics, flavonoids, phytic acid and tannin content • MFs showed higher SDS and lower RDS compared to WF • pGI of MFs ranged from 40.17 to 52.49, while for wheat flour was 62.59 • Phytic acid and tannin decreased the dough development	(Sharma & Gujral, 2019b)

Here RS: Resistant starch; eGI: expected glycemic index; RDS: rapid digestible starch; SDS: slowly digestible starch; IGP: inherent glycemic potential; CLSM: confocal laser scanning electron microscopy; PA: palmitic acid; OA: oleic acid; LA: linoleic acid; ALC: amylose–lipid complexes; FiM: Finger millet; FoM: Foxtail millet; KM: Kodo millet; LM: Little millet; PrM: Proso millet; PM: Pearl millet; KuM: Kutki millet MF: Millet flour; pGI: predicted glycemic index; TDF: Total dietary fiber; IVPD: In vitro protein digestibility; WF: wheat flour; SPI: soy protein isolate; WPI: whey protein isolate; PV: Peak viscosity; DDT: dough development time; WAC: Water absorption capacity; FV: Final viscosity; SB: Setback; BD: Breakdown; PT: Pasting temperature; TV: Trough viscosity; PV: Peak viscosity; Lys: lysine; Thr: threonine; Asp: aspartic acid; DC: Degree of crosslinking; SP: Swelling power; PMPo: pearl millet porridge; PMCo: pearl millet couscous; PrMPo: proso millet porridge; PrMCo: proso millet couscous; DSC: differential scanning calorimetry; DF: dietary fiber; GI: glycaemic.

significantly alter the RS content. Also, a further increase in DF marginally increased the RS. The probable reason could be the higher water holding capacity of DF, which can restrict starch hydration, decreasing the millet starch gelatinization, eventually increasing the starch crystallinity (Agama-Acevedo et al., 2012). Furthermore, higher DF content could trap starch inside the pores, thereby obstructing hydrolysis (Oh et al., 2014). Another study was aimed to assess the effect of biological processing techniques on bio-and technofunctional characteristics of foxtail millet (Sharma & Sharma, 2022). The millet grains were exposed to fermentation, germination, and soaking. A substantial variation in the in vitro protein and starch digestibility, bioactive composition, and antioxidant potential was observed. The bioprocessed flours exhibited altered functional properties due to the hydrolytic action of activated enzymes. The bioprocessed flours exhibited a degraded protein matrix; while, only fermentation and combination treatments hydrolyzed the granular millet starch.

In another study, the effect of protease, xylanase and glucose oxidase enzymes was studied on the sensory, pasting, rheological, and textural quality of gluten-free foxtail millet bread (Sarabhai et al., 2021). The presence of these enzymes in the millet food matrix substantially increased the crumb springiness and specific volume while reducing the crumb cohesiveness and hardness in comparison to control. Enzyme addition also changed the rheological properties of the millet bread batter. All parameters evaluated under pasting properties significantly increased when compared to the control. The decrease in peak temperature due to protease treatment results in a continuous structure development in the millet bread crumbs and further assists in the re-aggregation of starch granules. With respect to sensory properties, the bread added with protease has a superior taste, aroma and quality.

Antinutrients like tannin and phytic acids can lower the dough development of millet flour due to their interaction with the protein surface. They also decrease the susceptibility of protein and starch to enzyme-mediated hydrolysis in the GIT. Phytic acid exhibits a protective effect by preventing the disintegration of the starch paste under mechanical shearing. Similar results were reported on millet starch by (Sharma & Gujral, 2019b). Lutein (β, ε-carotene-3,3′-diol) is a lipophilic, yellow-orange crystalline solid having a conjugated carbon–carbon double bond backbone which permits the movement of free electrons. It is a member of the xanthophyll carotenoid family and is predominant in fruits, flowers, grains and vegetables (Yang et al., 2018). Lutein is an efficacious functional compound that is highly beneficial to human health due to its high antioxidant potential and ability to mitigate cardiovascular ailments (Dwyer et al., 2001), malignancy (Heber & Lu, 2002), muscle degradation due to ageing (Landrum & Bone, 2001), maintenance of eye health, as a Pro-Vitamin A. Despite these merits, its use is limited in the food industries due to structural instability and chemical alterations during processing (Qv et al., 2011). Since the physical state of the food matrix chiefly determines its bioavailability. It is important to ensure the maintenance of lutein integrity throughout food processing and increase their bioavailability and accessibility from the food matrix. For lutein to be bioavailable it must be liberated from the food matrix, absorbed through intestinal enterocytes and transported to the target tissues. Since lutein is a lipophilic compound it is emulsified into tiny lipid droplets which are then integrated into mixed micelles which are then absorbed by the enterocytes (Xavier et al., 2018). Studies suggest that an increase in the fat component of the food matrix increases lutein bioavailability since it assists its absorption (Ochoa Becerra et al., 2020). Cooking zeaxanthin and lutein-rich foxtail

millets cause the paling of its colour after cooking, decreasing its appearance (Shen et al., 2015). The colour change was due to the carotenoid degradation during high-pressure and micro-pressure cooking while atmospheric-pressure cooking resulted in greater retention of yellow pigments. The retention of pigments during atmospheric-pressure cooking could be related to the protective effect of macromolecular food matrix components since a number of carotenoids are non-covalently integrated with fibre or proteins, dissolved in oils or as crystalline structures (Parada & Aguilera, 2007). These interactions between the carotenoids and macromolecules in the food matrices help to protect carotenoids during cooking and processing.

Pearl millet grains were mixed with carrot powder (provitamin A), leaf powder of *Moringa oleifera* (Moringa) (rich in iron) and *Adansonia digitata* (Baobab) and extruded to make instant cereal porridges. These nutritionally rich extrudates were further accessed for the effect of interactions in the complex food matrix on nutrient bioaccessibility, retention and stability (Ndiaye et al., 2020). These blends exhibited a high bioavailability of provitamin A, suggesting the nutritional and functional benefits of plant-based materials that can be developed into edible products with pearl millet as the main component. Studies on various matrix interactions in millet based foods are summarized in Table 1.

5. Conclusion and future prospectives

The notion of food matrix has been thoroughly used by nutritionists and food scientists to explain the distinct behaviour of nutrients in a solution or isolated conformation. Several matrices have been recognized in foods and categorized as polymer networks, cellular tissues, emulsions, and liquids. In the field of food technology, the food matrix determines the structure and subsequently, the texture, breakdown in mouth, flavour release, appearance, nutritional bioavailability and accessibility. Analytical procedures used for accessing the nutrient bioaccessibility and bioavailability should contemplate the matrix effects for representing highly accurate results. Engineering the food matrix structure that ensnares, protect and regulates the nutrient release can form the future basis for a rational healthy food design. A more meticulous approach to characterize the food matrix and their association with other food components could improve the perception of their roles in the functionality of products, development of highly accurate in vitro and in vivo models for nutritional assessment. Nutrition and food science should accept novel testing procedures and strategies, replacing a single nutrient approach with focusing on real food and dietary patterns.

Binary and ternary interactions substantially determine the digestibility and functionality of food and the bioavailability of nutrients. The formation of a complex between the matrix components significantly influences the nutritional quality and physicochemical properties of starch-based foods. Starch-lipid complex formation during the processing of food prevents the starch retrogradation and subsequently, staling of bread. Interactions between starch lipid and protein complexes resist the enzymic digestion of starch, attenuating the glycemic response of the food. Besides the processing perspectives of these interactions, the binary and ternary complex can have use in food industries due to their distinct functional properties like good plasticity, high viscosity and nongelling behaviour. Particularly, starch-protein-lipid and starch-lipid complexes can be potentially used as a fat replacement in low-calorie diet foods. Furthermore, the RS formed by starch-protein-lipid and starch-lipid complex can be utilized as nutritionally relevant functional ingredients in functional foods.

Interactions between polyphenols and proteins can potentially influence the amino acid bioavailability and modification in the protein structure could influence the digestibility and functionality of proteins. Phenol-protein interactions also affect the bioavailability and antioxidant activities of phenols by functioning as carriers of polyphenols through the GIT and protection from oxidation reactions. Interactions between polyphenols and lipids can decrease fat absorption and shield

polyphenols during their passage through the GIT. Also, the deleterious effect of lipid peroxidation products can be prevented by phenol-lipid interactions.

The vacant lumen inside the amylose helices of the starch-protein-lipid and the starch-lipid complexes can accommodate small hydrophobic bioactive molecules of low solubility for their target-specific delivery and regulated release. The formation of binary and ternary complexes is influenced by several factors, like the type of lipid (saturation), starch (amylose and amylopectin content), type of amino acids in a protein and processing method used. Conceptualizing and understanding these determining factors could assist the use of these complexes, in designing specific food types. However, the development of reliable techniques for effective quantification of these complexes for their use as food ingredients and to establish the association between the functional properties of these complexes and that of foods containing them is still an important area for future research. The increasingly high prevalence of diet and lifestyle-related diseases, the superior prebiotic properties and the low digestibility of starch-lipid complex have drawn a lot of attention recently. In this regard, the possible health benefits of these binary and ternary complexes, particularly their prebiotic properties, are a critical area for future investigations.

CRediT authorship contribution statement

Maharishi Tomar: Writing – original draft, Conceptualization, Visualization. **Rakesh Bhardwaj:** Supervision, Writing – review & editing. **Reetu Verma:** Supervision, Writing – review & editing. **Sumer Pal Singh:** Supervision, Writing – review & editing. **Anil dahuja:** Supervision, Writing – review & editing. **Veda Krishnan:** Supervision, Writing – review & editing. **Rekha Kansal:** Supervision, Writing – review & editing. **Vijay Kumar Yadav:** Supervision, Writing – review & editing. **Shelly Praveen:** Supervision, Writing – review & editing. **Archana Sachdev:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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