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CENTENARY REVIEW

Do kafirin bioplastic materials have unique functional characteristics?

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Abstract

Background and Objectives: There is considerable interest in kafirin, sorghum prolamin, as a bioplastic material because it apparently produces bioplastics with superior functional properties. This review evaluates the evidence, focussing on research directly comparing the properties of kafirin bioplastics (films and elastomers) with those from zein and gluten.

Findings: Kafirin and zein are more hydrophobic than gluten but there is little difference in hydrophobicity between them. Kafirin and zein films have better moisture barrier properties than gluten films. Films made from total kafirin (α-, β-, and γ-kafirins) are stronger and take up less moisture than films from commercial zein (essentially α-zein). However, total kafirin- and total zein films have similar moisture uptake. Also, there is little difference in oxygen barrier properties between total kafirin- and commercial zein films. Total kafirin elastomers have better elastic recovery than commercial- and total zein elastomers and similar elastic recovery to gluten.

Conclusions: The better functional properties of kafirin bioplastics compared to commercial zein bioplastics seems to be largely due to the greater disulfide bonded polymerization of kafirin polypeptides, involving the cysteine-rich β- and γ-kafirin classes.

Significance and Novelty: This work should stimulate research into disulfide-bonded polymerization of prolamins to improve their bioplastic functionality.

KEYWORDS

bioplastics, disulfide bond crosslinking, gluten, hydrophobicity, kafirin, zein

1 | INTRODUCTION

According to Osborne (1909), the first mention that sorghum grain contained a considerable quantity of an alcohol-soluble protein was by Kreusler, sometime after 1869. However, the first detailed study of kafirin was by Johns and Brewster (1916). These authors coined the name kafirin from "kafir corn," the then common English name for sorghum. Among the several important findings made by Johns and Brewster were that kafirin closely resembled zein (the maize prolamin) in terms of its elemental composition. However, they observed that whereas zein was readily soluble in 70% ethanol at all

temperatures, kafirin was only poorly soluble in ambient-temperature aqueous ethanol but was more soluble in hot solution. An apparently significant observation with regard to kafirin's functionality was that an aqueous-ethanol solution would gel on cooling, even at low concentration.

Since the 1970s, there has been a vast increase in research into the proteins of sorghum. This was initially driven to a large extent through work to improve the protein nutritional quality of sorghum, in particular, through the development of high-lysine genotypes that have downregulated and altered kafirin synthesis (Benmoussa et al., 2015; Paulis & Wall, 1979). More recently, the majority of kafirin research has concerned its potential as a functional protein in food and nonfood applications, particularly in nonwheat and gluten-free bakery products and as a bioplastic material (see e.g., reviews by Bean et al., 2019; Xiao et al., 2017). The motivation for much of this more recent research is the concept that kafirin has superior functional properties for such applications even compared with other prolamins. For example, Xiao et al. (2015) state that kafirin is relatively more hydrophobic and less digestible than zein, and Huang et al. (2020) state that kafirin exhibits superior water, gas, and lipid barrier properties. Both refer to works by this present author and co-workers (Duodu et al., 2003; Emmambux et al., 2004; Taylor et al., 2006).

The issue as to whether kafirin has uniquely valuable functional attributes for these applications is fundamentally important for two reasons. First, with general regard to prolamins, despite well over a century of research into prolamins as bioplastic materials (Krull & Inglett, 1971; Lawton, 2002) and 30 years of research into zein as a functional visco-elastic protein in bread (Lawton, 1992), their commercial application is minimal. Second, with specific respect to kafirin, any unique functional attributes that it has need to significantly outweigh the drawbacks of sorghum as a prolamin feedstock. For example, sorghum is not currently used to produce starch commercially, unlike maize and wheat, which generates prolamin or prolamin-enriched protein as a co-product. Also, with regard to bioethanol production whereby the distillers dried grain, which is concentrated in prolamin, could be used as feedstock, the amount produced from sorghum is very small. In the United States, which is by far the largest grain bioethanol producer, it constitutes only about 3% of the quantity of maize used (Sorghum Checkoff, 2022; U.S. Department of Energy, 2021).

This review first compares the relevant physico-chemical characteristics of kafirin to those of other prolamins. Then it critically reviews research, where available, that directly compares the functionalities of kafirin bioplastics relative to those from zein, wheat gluten, and common synthetic plastics. The review concludes by evaluating the available evidence as to whether kafirin bioplastic materials have unique functionalities and if so why.

2 | KAFIRIN

2.1 | Composition and structure

The chemical composition and structure of kafirin has been comprehensively reviewed elsewhere. See Belton et al. (2006), Bean and Ioerger (2015), Taylor and Taylor (2017), and Bean et al. (2019). Here, the salient points are briefly summarized for the benefit of the nonsubject matter specialist. Three different classes of kafirin polypeptides are expressed, α-, β-, and γ-. These polypeptides are quite small, with relative molecular masses ranging from approximately 16–18k (β-), 23–25k (α-) to 28k (γ-) (Shewry, 2002). The α-kafirins are most abundant, approximately 80%, followed by γ- 9%–12% and β- 7%–8%. Like all prolamins, the kafirins are rich in glutamine and proline. Kafirins are also rich in the hydrophobic amino acids alanine and leucine. Importantly, the γ- and β- classes are also rich in cysteine, the sulfhydryl (SH) group containing amino acid. The γ-class is also rich in histidine. In the grain, kafirins are polymerized into oligomers and polymers by disulfide bonding, with different proportions of the classes (El Nour et al., 1998). The kafirin classes are very closely homologous in terms of amino acid composition, electrophoretic pattern, and amino acid sequences with the same classes that comprise zein (Belton et al., 2006; Shull et al., 1991). Zein also polymerizes by disulfide bonding but there is direct evidence that kafirin is polymerized to a greater degree (Emmambux & Taylor, 2009). Kafirin (kafirin-1 type, i.e., extracted using aqueous alcohol in the absence of a reducing agent) in aqueous alcoholic solutions has a predominantly α-helical structure, whereas with dry kafirin although the main secondary structure is α-helical (49%), it also has substantial β-turn (27%) and β-sheet (24%) conformations (Xiao et al., 2015). Values calculated from their amino acid sequences also revealed that the main secondary structure of the three kafirin classes was α-helical but that random coli was the second largest conformation (Dianda et al., 2019). Hence, the general secondary structure of kafirin is similar to zein, which has been studied in much detail, with α-zein having some 40%–60% α-helical conformation (Cabra et al., 2006).

2.2 | Thermal properties

The very limited literature on the thermal properties of kafirin clearly reveals that some transitions take place. Notably, however, there is no agreement as to its glass transition temperature (T_g), with values ranging from 40°C to 233.8°C having been reported (Table 1). The latter value was found by two independent research teams (Mahajan & Mhaske, 2020; Wang et al., 2009). A similar wide range of T_g has been reported for films made from kafirin alone (i.e., without inclusion of plasticizers), −2.5°C to approximately 150°C. With one exception, all the data were obtained using differential scanning calorimetry. Thus, these very large differences are not attributable to fundamental differences in the analytical instrumentation used. Two related reasons for the discrepancies seem probable: (1) the presence of other substances in the kafirin preparations analyzed, most importantly moisture which dramatically reduces the T_g of prolamins (Lawton, 1992; Noel et al., 1995) and other proteins by plasticizing them (Matveev et al., 2000). (2) Differing interpretations of the data with respect to whether an observed endotherm or frequency oscillation represented the kafirin glass transition. Hence, it is not possible to state categorically whether the T_g of kafirin is higher or lower than those of zein and wheat gluten. However, the majority of kafirin protein data indicate that kafirin's T_g is higher.

There is also no agreement as to whether plasticization of cast kafirin films lowers or raises the T_g (Table 1), although the former is logical (see below). Plasticization involves the inclusion of nonvolatile, low molecular weight compounds together with the polymer material to improve the flexibility and mechanical properties of the plastic (Banker, 1966). The term "cast films" is explained in Section 3. Where there is agreement is that kafirin undergoes irreversible thermal degradation (pyrolysis) at a temperature of 270–290°C. Significantly, this temperature is only slightly higher than the highest T_g reported and the melting temperature values reported, approximately 234°C and 249–251°C, respectively, but some 60°C and 110°C higher than the melting temperatures of the common thermoplastics low-density polyethylene (LDPE) and polypropylene (PP), respectively (United States Documents, 2020). To make both kafirin and zein behave as thermoplastics it is necessary to plasticize them (S. Iannace, Italian Research Council, personal communication). This is unlike the situation with polyethylene and PP, but like polyvinyl chloride (Cadogan & Howick, 2012). Di Maio et al. (2010) showed that when shear is applied, kafirin plasticized with 25% polyethylene glycol melted at a temperature of about 110°C and when plasticized with 25% lactic acid at <70°C. The tensile properties of the plasticized kafirin were similar to those of plasticized commercial zein, which is essentially just α-zein (Taylor et al., 2018; Wilson, 1988; Xiao et al., 2015), with kafirin having a tensile modulus (stiffness) up to 750 MPa and a tensile strength of 10 MPa and strain at break of up to 50%. The tensile modulus of the plasticized kafirin was therefore similar to that of high-density polyethylene but it was somewhat weaker and less extensible.

2.3 | Hydrophobicity

There are several ways of calculating the hydrophobicity/hydrophilicity of a protein. Probably the most commonly used are free energy of hydration and GRAVY (Grand average of hydropathicity index). Free energy of hydration is the energy released when one mole of an ion undergoes hydration. With proteins, it is calculated by summing up the free energies of all the amino acids in a protein in terms of their mole percent. The less negative the value, the more hydrophobic the protein. GRAVY is calculated as the sum of the hydropathy values of all the amino acids divided by the polypeptide sequence length. Proteins with positive indexes are hydrophobic. Both the free energy of hydration and GRAVY values indicate that the kafirin and zein classes are more hydrophobic than the gliadins and glutenins (Table 2). The very high content of glutamine, 30–50 mole% in the gluten proteins, approximately twice that in the kafirins (Belton et al., 2006) and zeins (Lawton & Wilson, 2003), is probably the major reason that the gluten proteins are less hydrophobic.

The data do not, however, clearly indicate that kafirin is more hydrophobic than zein, and are somewhat contradictory. Concerning the α-classes, the free energy of hydration values are the same for α-kafirin and α-zein and the GRAVY value is slightly higher for α-zein. There are widely varying data for the free energy of hydration of β-kafirin. Both the free energy of hydration and GRAVY data indicate that γ-kafirin is slightly more hydrophobic than γ-zein. However, the free energy of hydration values indicate that γ-kafirin and γ-zein are the most hydrophobic of the kafirin and zein classes, whereas GRAVY indicates that they are the least hydrophobic. The latter is consistent with the fact that their monomeric forms are water-soluble (Evans et al., 1987; Wilson et al., 1981). The reader is referred to Schober et al. (2011) for a more in-depth discussion of factors affecting the hydrophobicity of kafirin and zein.

A property related to the hydrophobicity of proteins is their electrokinetic potential in colloidal suspension, commonly measured as zeta potential. As shown in

TABLE 1 Thermal properties of the kafirin compared with those of zein and gluten.

Protein	Form of material	T_g (°C)	T_m (°C)	Thermal degradation temp. (°C)	Analysis technique	Reference
Kafirin (probably lacking γ-kafirin)	Cast film alone Including 40% glycerol plasticizer	Approx. 150 Approx. 65			DSC	Gao et al. (2006)
Kafirin (α- and β-kafirins, and probably γ-kafirin)	Protein	227.9–233.8		≥270–290	DSC	Wang et al. (2009)
Total kafirin	Protein	41			DMA	Schober et al. (2011)
Total kafirin	Protein	233.79			DSC	Mahajan and Mhaske (2020)
Total kafirin γ-kafirin	Protein Microparticles Protein		248.6 253.9 270.5		DSC	Anyango et al. (2013)
Kafirin (no compositional information)	Cast film alone Including 40% polyethylene glycol plasticizer	−2.7 −10.9	68.4 100.5	287.9 289.5 (temp. of max. pyrolysis)	DSC	Lal et al. (2017)
Kafirin (no compositional information)	Cast film alone Including 40% polyethylene glycol plasticizer	75.33 56.88			DSC	Patil et al. (2021)
Zein (zein-1 type)	Protein	160–167			DSC	Di Gioia et al. (1999)
Gluten (various gliadins and glutenins)	Protein	124–145 Approx. 27 when plasticized with 10% water			DSC	Noel et al. (1995)

Abbreviations: DMA, dynamic mechanical analysis; DSC, differential scanning calorimetry; T_g, glass transition temperature; T_m, melting temperature.

TABLE 2 Hydrophobicity of the kafirin, zein, and gliadin classes and glutenin.

Prolamin	Free energy of hydration (kcal/mole)	References	GRAVY	References	Zeta-potential	References
α-kafirin	−140.360	Duodu et al. (2003)	0.193	Schober et al. (2011)		
β-kafirin	−123 −166.500	Belton et al. (2006) Ncube et al. (2022)	0.170			
γ-kafirin	−113.630	Duodu et al. (2003)	−0.227			
Total kafirin					−7.5 (in water) −16.4 (in 0.1 M NaOH)	Teklehaimanot and Emmambux (2019)
α-zein	−139.780	Duodu et al. (2003)	0.238	Schober et al. (2011)		
β-zein	−135.946	Calculated from Pederson et al. (1986)	−0.091			
γ-zein	−124.520	Duodu et al. (2003)	−0.336			
Total zein					−7.1 (in water −24.5) (in 0.1 M NaOH)	Teklehaimanot and Emmambux (2019)
α-gliadin			−1.002	Jang et al. (2020)		
γ-gliadin	−147.102	Cabra et al. (2006)	−0.849 −0.681	Jang et al. (2020) Cabra et al. (2006)		
ω-gliadin	No data	No data	−1.608	Jang et al. (2020)		
Gliadin	−159.794	Shewry et al. (2003)	No data			
Glutenin	−165.817 −163.258	Shewry et al. (2003) Cabra et al. (2006)	−0.715	Cabra et al. (2006)		

Abbreviation: GRAVY, Grand average of hydropathicity index.

Table 2, total kafirin and total zein (i.e., kafirin and zein preparations comprising the α-, β-, and γ- classes) were found to have the same zeta potential in water but zein was more negatively charged in dilute NaOH. This suggests that kafirin is slightly less hydrophilic than zein, albeit at high pH, and could hydrogen bond with water to a smaller degree.

3 | PROPERTIES OF KAFIRIN BIOPLASTIC MATERIALS

Kafirin and the other prolamins can be formed into numerous different types of bioplastic materials. In the case of kafirin, see for example: cast films (Buffo et al., 1997), coatings (Buchner et al., 2011), spun fibers (Xiao et al., 2016), elastomers (Oom et al., 2008), hydrogels (Xiao et al., 2017), molded thermoplastics (Di Maio et al., 2010), microparticles (Taylor et al., 2009), and nanoparticles (Xiao et al., 2016).

With kafirin, most interest has centered on cast films and elastomers, and hence these will be the focus of this review. To date, kafirin films have been essentially exclusively prepared by casting. Film casting involves dissolving the protein in a solvent, an organic solvent in the case of kafirin and other prolamins, and evaporating the solvent off on a flat surface to produce a film. The technique differs from that used to produce most synthetic plastic films where the polymer is melted at elevated temperature then stretched and blown with air to create a very thin film (Amcor, 2020). Zein films have been blown (Oliviero et al., 2010). To date, blowing of kafirin films has not been reported. The term elastomer refers to polymers that exhibit rubber-like elasticity or visco-elasticity (De Sadkan & White, 2001). Here, it is used to embrace various other terms that have been used

with respect to such materials made from prolamins, for example, gluten (Delcour & Hoseney, 2010), dough (King et al., 2016), macropolymer (Schober et al., 2011), visco-elastic mass (Elhassan et al., 2018), and resin (Lai & Padua, 1997). To make such prolamin elastomers they must be highly plasticized. Water is the normal plasticizer in wheat gluten. With kafirin and zein, organic plasticizers such as acetic acid (Elhassan et al., 2018), lactic acid (Sly et al., 2014), or dibutyl tartrate (Lawton, 1992) are additionally included. With resins, water plus fatty acids such as oleic acid are used as the plasticizer (Oom et al., 2008). With prolamin films, they must also be plasticized to make them flexible and a wide variety of organic compounds have been used as plasticizers. In the case of kafirin, glycerol, lactic acid, and polyethylene glycol and their combinations are most commonly used. See for example: Buffo et al. (1997), Byaruhanga et al. (2006), Giteru et al. (2015), and Lal et al. (2017). Obviously, the amounts and types of plasticizers included have a profound effect on the functional properties of prolamin films and elastomers. Comparison between different prolamins has to take this into consideration and consequently trends are more meaningful than actual values. Also, because of differences in methodology between studies, this review focuses on studies which directly compared the properties of these bioplastic materials when made from different prolamins.

3.1 | Mechanical properties

Data on prolamin films shows that cast zein films have a similar strength as common synthetic polymer films such as LDPE but are far less extensible, despite their inclusion of plasticizers (Krochta, 2002). We have observed the same for both kafirin and zein films (unpublished). Research comparing the tensile properties of kafirin and zeins films shows an apparent discrepancy. Da Silva and Taylor (2005) and Gillgren and Stading (2008) found that cast kafirin films were stronger and less extensible than films made from commercial zein (Table 3). In contrast, Buffo et al. (1997) found little difference and Gao et al. (2005) found that there was a difference with films made from kafirin extracted with aqueous ethanol plus sodium metabisulfite as reducing agent but not with films from kafirin extracted with aqueous tertiary butanol plus dithiothreitol as reducing agent. The probable reason is that the former authors both studied films made from kafirin that had been extracted in the presence of a reducing agent and as such would comprise total kafirin, whereas Buffo et al. (1997) used kafirin extracted without a reducing agent. As mentioned above, extraction without a reducing agent yields what is referred to as kafirin-1, which lacks some of the disulfide-bonded polymers (De Mesa-Stonestreet et al., 2010). The findings of Gao et al. (2005) can be explained by the particular extraction procedure used with the reducing agent dithiothreitol, which probably resulted in the dithiothreitol remaining in the kafirin preparation, thus preventing reformation of disulfide crosslinking. Taken together, these data suggest that the disulfide-bonded polymers contribute to prolamin film strength but limit extensibility. In support of this was the observation that elastomers made from total zein, which contained the cysteine-rich β- and γ-zeins as well as α-zein, were far less extensible than those made from commercial zein (King et al., 2016).

The one study that compared the properties of kafirin and zein molded thermoplastics, which were in the form of thin sheets, indicated that plasticizer type was the major factor influencing their tensile properties (Di Maio et al., 2010). When polyethylene glycol was used as the plasticizer, the total kafirin thermoplastic was stronger and less extensible than the commercial zein thermoplastic but when lactic acid was used, the opposite was the case (Table 3). These effects may have been due to the fact that lactic acid is a good solvent for kafirin, probably due to it being an amphoteric organic solvent (Taylor et al., 2005).

Concerning comparative studies of the mechanical properties of prolamin elastomers, the four studies showed that total kafirin has more elastic character than zein (Table 4). Further, the three studies from our laboratory showed that kafirin was much more elastic (higher % stress-recovery) than both total zein and commercial zein and that kafirin had a similar percentage stress-recovery to vital wheat gluten. Vital gluten is gluten that has been isolated in such a way as to retain its visco-elastic character.

This difference between total kafirin and total zein was observed over a very wide range of acetic acid plasticizer concentrations, from 33% down to 0.1%. The fact that total kafirin had greater elasticity than total zein and similar to that of gluten may be attributable to the fact that the 19 and 22 kDa α-kafirin polypeptides both have an additional cysteine residue compared with their zein homologs (Belton et al., 2006). The additional cysteine residues could have facilitated greater disulfide-bonded crosslinking, thus strengthening the kafirin elastomers (Oguntoyinbo et al., 2018).

The studies also indicated that there were differences in elasticity between different types of kafirin, which were possibly attributable to their degree of disulfide bonding (Taylor et al., 2018) and hydrophobicity (Ncube et al., 2022), which in turn resulted from differences in

TABLE 3 Comparison of the mechanical properties of kafirin and commercial zein films and sheets.

Prolamin	Source	Plasticizer			References
			Tensile strength (MPa)	**Elongation at break (%)**	Buffo et al. (1997)[a]
Kafirin (kafirin-1)	Sorghum gluten	Glycerol + PEG (32%)	2.1	106.1	
Zein (commercial—essentially α-zein)	Yellow maize		2.6	84.4	
			Tensile strength at break (N/mm^2)	**Strain at break (%)**	Da Silva and Taylor (2005)[a]
Kafirin (total)	Whole-grain red nontannin cultivar	Glycerol + PEG + lactic acid (42%)	5.5	35.3	
	Wholegrain white nontannin cultivar		7.4	23.5	
Zein (commercial—essentially α-zein)	Yellow maize		2.3	127.1	
			Tensile stress at break (MPa)[b]	**Strain at break (%)**[b]	
Kafirin (total) (extracted with aqueous tert-butanol + DTT)	Wholegrain white nontannin cultivar	Glycerol + PEG (32%)	2.0	146.1	Gao et al. (2005)[a]
Kafirin (total) (extracted with aqueous ethanol + SMS)	Wholegrain white nontannin cultivar		4.3	16.7	
Zein (commercial—essentially α-zein)	Yellow maize		1.8	203.0	
			Tensile stress at break (MPa)	**Strain at break (%)**	Gillgren and Stading (2008)[a]
Kafirin (total)	Red nontannin cultivar	Glycerol (20%	20.9	1.6	
		Glycerol (30%)	9.3	3.3	
		Glycerol (40%)	3.5	35.8	
Zein (commercial—essentially α-zein)	Yellow maize	Glycerol + PEG (20%)	16.3	1.6	
		Glycerol + PEG (30%)	6.4	6.4	
		Glycerol + PEG (40%)	3.5	116.7	

(Continues)

TABLE 3 (Continued)

Prolamin	Source	Plasticizer	Tensile strength (MPa)	Strain at break (mm/mm)	References
Kafirin (total)	Red nontannin cultivar	PEG (25%)	9.0	0.089	Di Maio et al. (2010)[c]
		Lactic acid (25%)	6.3	0.504	
Zein (commercial—essentially α-zein)	Yellow maize	PEG (25%)	2.7	0.120	
		Lactic acid (25%)	16.4	0.043	

Abbreviations: DTT, dithiotheitol; PEG, polyethylene glycol; SMS, sodium metabisulfite.
[a]Cast films.
[b]Average of four slightly different treatments.
[c]Molded thermoplastic sheets (0.3–0.5 mm thick).

the proportions of the different kafirin classes. Additionally, the research of Ncube et al. (2022) showed that with model doughs (blends of the prolamin elastomers plus corn starch), the model dough made from a blend of commercial zein with kafirin was stronger and less extensible than dough made with a blend commercial zein and total zein. This finding similarly suggested that the greater disulfide bond crosslinking of the kafirin was involved.

3.2 | Bioplastic water/moisture barrier properties

A practical way of estimating the relative hydrophobicity of prolamin plastics is to simply soak films in water or buffer and measure liquid uptake. This test is also indicative of the water barrier properties of their films. A complication with regard to interpretation of the data is that most of this research has been carried out using films prepared with high proportions of water-soluble plasticizers, see for example Soliman et al. (2009), Anyango et al. (2011), and Lal et al. (2017). Table 5 shows that when cast films were prepared without plasticizer, the kafirin and zein films took up much less buffer than films made from vital gluten, which is consistent with the greater hydrophobicity of kafirin and zein (Table 1). This in turn is probably primarily due to kafirin (Shewry, 2002) and zein (Lawton & Wilson, 2003) both containing less glutamine and more hydrophobic amino acids such as alanine and leucine. The data in Table 5 also show that heat-treating all the cast prolamin films or making kafirin films from kafirin extracted from distillers dried grain and solubles, which had been heated to dry it, resulted in a considerable reduction in buffer uptake. Research on heat-treated cast kafirin and zein films prepared with water-soluble plasticizers by Byaruhanga et al. (2005) and Han et al. (2014), respectively, also indicated this. We have proposed that the reduction in kafirin film buffer uptake by heat treatment is due to disulfide bonding (Muhiwa et al., 2017). Byaruhanga et al. (2005) observed a reduction in free SH groups and an increase in SS groups when both kafirin protein and kafirin films were heat treated and a corresponding reduction in film water vapor permeability. Simplistically, increased disulfide crosslinking could reduce prolamin film water uptake by restricting film swelling. However, as the reduction in buffer uptake also occurred in commercial zein films that had been heated-treated (Table 5), and, as stated, commercial zein is essentially just α-zein and hence

TABLE 4 Comparison of the mechanical properties of kafirin, zein, and wheat gluten elastomers.

Prolamin	Source	Plasticizer		References
			Storage modulus (G') (kPa)[a]	Oom et al. (2008)
Kafirin (total)	Red nontannin variety	Water + oleic acid	307	
Zein (commercial—essentially α-zein)	Yellow maize		117	
			% Stress-recovery[b]	Taylor et al.(2018)
Kafirin (total)	White nontannin variety	Approx. 33% Acetic acid solution	76.9	
Kafirin (high α-kafirin)			59.1	
Kafirin (minus γ-kafirin)			32.3	
Kafirin (high α-kafirin minus γ-kafirin)			32.1	
Zein (total)	White cultivar		26.4	
Zein (high α-zein)			31.2	
Zein (commercial—essentially α-zein)	Yellow cultivar		21.8	
Wheat gluten (vital)	Commercial	Water	43.3	
			% Stress-recovery[c]	Oguntoyinbo et al. (2018)
Kafirin (total)	White nontannin cultivar	0.1% Acetic acid solution	44.1	
Zein (total)	White cultivar		17.2	
Wheat gluten (vital)	Commercial	Water	42.2	
			% Stress-recovery[d]	Ncube et al. (2022)
Kafirin (total)	White nontannin variety	3% Acetic acid solution	38.9	
Kafirin (total)	Waxy-normal protein digestibility variety		29.7	
Kafirin total	Waxy-high protein digestibility variety		52.7	
Zein (total)	White cultivar		8.6	
Wheat gluten (vital)	Commercial	Water	33.2	

[a]Fresh.
[b]After 16 days storage at 4°C.
[c]After 2 days storage at 4°C.
[d]After 7 days storage at 4°C.

lacks the cysteine-rich β- and γ- classes, this unlikely to be the complete explanation. Heat treatment also causes a reduction in α-helical secondary conformation and a corresponding increase in β-sheet conformation in kafirin and kafirin films (Byaruhanga et al., 2005) and similarly, with α-zein a reduction in α-helical conformation and an increase in β-sheet and random coil structure (Cabra et al., 2006). The Argos et al. (1982) structural model for zein proteins emphasized that the polar amino acid residues distributed along the α-helical surfaces allow intra- and intermolecular hydrogen bonding. Hence, a reduction in α-helical conformation could make the prolamins more hydrophobic.

Comparison of unplasticized kafirin and zein film water uptake also shows that total kafirin and total zein films took up less buffer than commercial zein films (Table 5). This may be attributable to restriction of film expansion caused by greater disulfide bonding in the former. Importantly, with respect to this, the data, albeit very limited, indicate that there was little difference in buffer uptake between total kafirin and total zein films.

TABLE 5 Buffer uptake by cast prolamin films prepared without plasticizer (% dry basis).

Prolamin	Source	Films dried at 50°C	Films post-heat treated at 130°C	References
Kafirin total)	Flour, Red nontannin cultivar	58.7	39.7 (32%)[a]	Sly (2019)
Zein (total)	White maize meal	74.4	39.1 (47%)	
Zein (commercial—essentially α-zein)	Yellow maize	81.4	60.9 (25%)	
Wheat gluten (vital)	Commercial	198.5	155.7 (23%)	
Kafirin (total)	Flour, Red nontannin cultivar	55.1	No data	Muhiwa et al. (2017)
Kafirin (total)	DDGS, Red nontannin cultivar	35.0	No data	
Zein (total)	White maize meal	58.9	No data	

Abbreviation: DDGS, Commercial sorghum distillers dried grain and soluble.
[a]Percentage reduction in buffer uptake with heat treating films.

Regarding the moisture and water vapor barrier properties of prolamin bioplastic films, research has been exclusively on films made with a high proportion of water-soluble plasticizers. Also, research has, with one exception, been limited to comparisons between kafirin and commercial zein films. The research shows that cast kafirin and commercial zein films did not differ substantially in their water vapor permeability (Table 6). However, this finding may be a consequence of the inclusion of the water-soluble plasticizers. The study by Gillgren and Stading (2008) also included a comparison with properties of films made from avenin, (oat prolamin). The water vapor permeability of avenin films was approximately twice that of the kafirin and commercial films. This may be attributable to avenin, like gluten, having a much higher content of glutamine (Wieser & Belitz, 1989) in comparison with kafirin and zein.

3.3 | Bioplastic oxygen barrier properties

There is sound evidence that cast plasticized commercial zein and gluten films are a much better oxygen barrier than polyethylenes (which are poor oxygen barriers) and approach the oxygen barrier properties of the synthetic plastics that are the best barriers, namely ethylene-vinyl alcohol copolymer and polyvinylidene chloride (Krochta, 2002). There is, however, only one comparative study between prolamin films (Gillgren & Stading, 2008). This showed that commercial zein was consistently a slightly better barrier than total kafirin over a wide range of plasticizer concentrations (20%–40%). Both were far better barriers than avenin. Several factors control the gas barrier properties of polymer films (Miller & Krochta, 1997). As the amino acid compositions and secondary structures of kafirin and commercial zein are very similar, the free volume of their films is likely to be an important factor as it can increase oxygen permeability rate by up to six orders of magnitude (Miller and Krochta, 1997). Possibly, the much greater disulfide bond cross linking in kafirin films resulted in areas of larger intermolecular free volume than in the commercial zein films. In this regard, Schober et al. (2011) produced data which indicated that weak, short-distance noncovalent bonding such as hydrophobic interactions, was responsible for the aggregation of kafirin and zein into elastomers and not disulfide bonding. Oguntoyinbo et al. (2018) alternatively proposed that hydrogen bonding was primarily responsible for holding the polymers together in such

TABLE 6 Comparison of the water vapor permeability of kafirin and commercial zein cast films.

Prolamin	Source	Plasticizer	Water vapor permeability[a]	References
Kafirin (kafirin-1)	Sorghum gluten	Glycerol + PEG (32%)	5.5	Buffo et al. (1997)
Zein (commercial— essentially α-zein)	Yellow maize		5.7	
Kafirin (total)	Whole-grain red nontannin variety	Glycerol + PEG+Lactic acid (42%)	0.60	Da Silva and Taylor (2005)
	Wholegrain white nontannin variety		0.57	
Zein (commercial—essentially α-zein)	Yellow maize		0.46	
Kafirin (total) (extracted with aqueous tert-butanol + DTT)	Wholegrain white nontannin cultivar	Glycerol + PEG (29%)	0.22	Gao et al. (2005)
Kafirin (total) (extracted with aqueous ethanol + SMS)	Wholegrain white nontannin cultivar		0.72[b]	
Zein (commercial—essentially α-zein)	Yellow maize		0.24	
Kafirin (total)	Flour white nontannin variety	Glycerol + PEG + Lactic acid (42%)	0.43	Taylor et al. (2005)
Zein (commercial—essentially α-zein)	Yellow maize		0.24	
Kafirin (total)	Red nontannin variety	Glycerol (20%	2.0	Gillgren and Stading (2008)
		Glycerol (30%)	2.9	
		Glycerol (40%)	2.9	
Zein (commercial—essentially α-zein)	Yellow maize	Glycerol + PEG (20%)	2.3	
		Glycerol + PEG (30%)	2.9	
		Glycerol + PEG (40%)	3.3	

Abbreviations: DTT, dithiotheitol; PEG, polyethylene glycol; SMS, sodium metabisulfite.

[a]g mm/m^2 h kPa.

[b]Average of four slightly different treatments.

kafirin and zein elastomers. However, the principle is still the same and is analogous to the situation with common synthetic plastics such as polyethylene where the polymers are held together by very weak dispersion forces (Peacock & Calhoun, 2006).

3.4 | Kafirin gelation

Despite the observation by Johns and Brewster (1916) that kafirin solutions gelled readily on cooling even at low concentration, there have been no systematic studies of this phenomenon in comparison to zein. However, it is well-known that zein gelation occurs readily at high concentration (20%–40%), normally within a day (Shukla & Cheryan, 2001). Kafirin gelation has been studied in research concerning formation of cast kafirin films. Gao et al. (2005) found that kafirin extracted with aqueous tertiary butanol plus reducing agent at 25°C, which had predominantly native α-helical conformation, dissolved readily in hot aqueous ethanol and formed uniform films. In contrast, kafirin extracted with aqueous ethanol plus reducing agent at 70°C dissolved poorly in hot aqueous ethanol and was prone to gelation, resulting in films of variable thickness. The kafirin extracted with tertiary butanol had a predominantly native α-helical conformation, whereas that extracted with aqueous ethanol had a higher intermolecular β-sheet content, indicating that the β-sheet conformation was associated with gel formation. In this regard, more recent work has indicated that solvent polarity influenced the secondary structure of cast kafirin films and their mechanical properties (Dianda et al., 2019). Probably also of relevance is the finding that dispersions of zein containing γ-zein (total zein) in aqueous ethanol exhibited gelation characteristics but no gelation was observed with samples of zein that did not contain γ-zein (Nonthanum et al., 2012). Furthermore, the inclusion of a reducing agent was found to decrease the time to gelation. The authors attributed this effect to unfolding and development of new polymer entanglements of the γ-zein peptides released by disulfide bond breakage. On the basis of this work, it is suggested that the presence of the γ-prolamin or its polypeptides freed by disulfide bond hydrolysis change kafirin and zein secondary structure, increasing β-sheet content. This in turn causes the proteins to gel. Hence, it seems likely that there is not a fundamental difference between kafirin and zein with respect to gelation behavior, rather it is the content of γ-prolamin in a particular kafirin or zein preparation.

3.5 | Biodegradability, biocompatibility, safety, and allergenicity

There is good evidence that cast total kafirin films are readily biodegradable. When subjected to a standard soil biodegradation test under aerobic conditions at around 50°C, the films were no longer functional within 5 days and almost complete destruction of the films took place within 4 weeks (Byaruhanga et al., 2005, 2007; Taylor et al., 2007). The rate of biodegradation of the kafirin films was similar to that of films made from commercial zein, despite the in vitro protein digestibility of the kafirin films being somewhat lower (Taylor et al., 2007). By contrast, LDPE films were unaffected over the 4-week period. The addition of condensed tannins to the kafirin during film casting considerably reduced in kafirin film in vitro digestibility and similarly slowed the rate of film biodegradation (Taylor et al., 2007), whereas heat-treatments had little effect (Byaruhanga et al., 2005, 2007). HPLC data indicated that the tannins bound preferentially to the γ-kafirin (Taylor et al., 2007). Unfortunately, these authors did not compare the effects of these treatments on zein films.

With bioplastics, degradability has to be balanced against durability depending on the application. A particularly challenging application is as implantable in-tissue biomaterials because not only do the implants have to have appropriate durability, for example, short for encapsulating bioactives and longer for tissue scaffolds, they also have to be safe and biocompatible. Taylor et al. (2015) investigated the effects of implanting porous total kafirin microparticles (bioactive encapsulation model) and cast hydrated total kafirin films (tissue scaffold model) subcutaneously in mice and rats, respectively. Quite different effects were observed. After 1-week postinjection, the microparticles were degraded. Further, they caused a severe chronic inflammatory response, more severe than with the polystyrene control sphere controls. It was suggested that this response was a result of the release of degradation products such as glutamate. In contrast, the kafirin films were only slightly degraded after 4 weeks (Figure 1) and were less degraded than the collagen control. Furthermore, the kafirin films did not cause any abnormal inflammatory reaction. The far slower rate of degradation and absence of an adverse response was attributed to the much smaller relative surface area of the kafirin films compared to the microparticles, which in turn resulted in less toxic degradation products. Probably the most similar zein study was where molded porous disks (scaffold model) made from commercial zein were implanted in rabbits (Wang et al., 2007). As with the kafirin films, no cytotoxicity was observed.

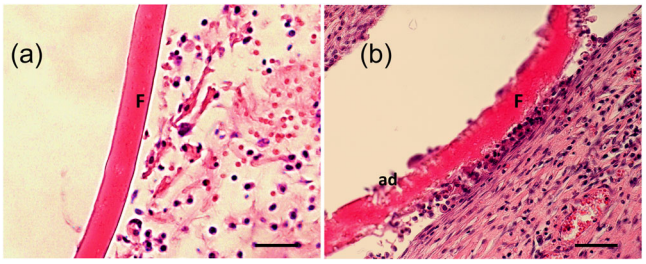

FIGURE 1 Light microscopy of the progress of degradation of kafirin film implants in rat tissue. Sections stained with hematoxylin–eosin. (a) 7 days after implant, (b) 28 days after implant. Scale bar = 100 μm. dg, areas of degradation; F, film.

With regard to safety in respect of food applications, zein has a Generally Recognized as Safe (GRAS) status from the U.S. Food and Drug Administration (1984). Kafirin does not as yet have GRAS status. However, there is very good evidence that wheat-free foods made from sorghum and hence containing kafirin are safe for consumption, even when consumed by persons suffering from celiac disease (Ciacci et al., 2007). Furthermore, the study also showed that digests of kafirin did not elicit any morphological or immunomediated changes in duodenal explants obtained from celiac patients, whereas adverse changes were observed with a gliadin digest positive control.

3.6 | Modification of kafirin bioplastic functionality

The bioplastic functionality of kafirin and other prolamins can be modified by physical and chemical treatments. With respect to kafirin, this topic has been reviewed elsewhere (De Mesa-Stonestreet et al., 2010; Taylor et al., 2013; Taylor & Taylor, 2018). The main treatment methods studied are: thermal treatment, which results in chemical crosslinking (as discussed in Section 3.2); chemical cross-linking using aldehydes, tannins and oxidizing agents; enzymatic cross-linking using transglutaminase and breakage of disulfide crosslinks using reducing agents. More recent research has investigated the effects of amidation and esterification on the mechanical properties of compression molded kafirin films (Mahajan & Mhaske, 2020). The films made from amidated kafirin had substantially lower water vapor permeability and somewhat greater tensile strength than the films made from untreated kafirin. The opposite was essentially the case with esterified kafirin films. An issue, however, is that such treatments can be applied to all prolamins and other proteins. So, unless there is a direct comparison between different prolamins (see Section 3.2 and Table 5), it cannot be concluded that a particular treatment imparts kafirin bioplastics with superior functional properties.

4 | CONCLUSIONS

The kafirin and zein proteins are substantially more hydrophobic than gluten and its gliadin equivalent proteins. This is primarily because of their higher proportion of hydrophobic amino acids such as alanine and leucine and lower proportion of glutamine. However, on the available evidence of both GRAVY and free energy of hydration data, kafirin is not clearly more hydrophobic than zein. Regarding the thermal properties of kafirin, essentially no firm conclusions can be drawn because of the very great range of reported values. This is probably as a consequence of analyses being performed with materials of different moisture contents and purity, and because of different interpretations of the identity of the transitions that were measured.

Regarding prolamin bioplastic mechanical properties, research shows that cast films made from total kafirin (α-, β-, and γ-kafirin) are stronger and but less extensible than those made from commercial zein (essentially just α-zein). Furthermore, there is good evidence that thermally induced disulfide cross-linking involving γ-kafirin increases the strength of kafirin films (Byaruhanga et al., 2006, 2007). Concerning the mechanical properties of total kafirin films versus and total zein films, unfortunately to date there have not been any direct comparative studies.

With regard to elastomers, total kafirin elastomers have higher stress-recovery than either commercial zein- and total zein elastomers, possibly also as a consequence of greater disulfide crosslinking (Oguntoyinbo et al., 2018). When the observed mechanical properties of films and elastomers are considered together, it seems likely that total kafirin bioplastics are stronger than total zein and commercial zein bioplastics, on account of kafirin's greater disulfide crosslinking. However, if kafirin was produced commercially by a steeping process involving treatment with sulfites, as is generally the case in commercial zein manufacture (Lawton, 2002), this would remove the γ-kafirin. The likely effect would be that the mechanical properties of these "commercial kafirin" bioplastic materials would not differ substantially from those of commercial zein bioplastic materials.

Concerning moisture barrier properties, kafirin and zein bioplastic films take up much less moisture than gluten films. This is presumably primarily due to kafirin and zein being more hydrophobic but perhaps additionally because they have a predominantly α-helical conformation, whereas gluten is predominantly in the

β-sheet conformation (Georget & Belton, 2006). Total kafirin films take up less moisture than commercial zein films. However, there seems to be little difference in moisture uptake between total kafirin and total zein films. As with mechanical properties, this seems to be primarily a consequence of disulfide bond crosslinking as heat treatment reduces film moisture uptake. It is not possible to draw any conclusions on the relative water vapor permeability of kafirin and zein films as all the directly comparative research to date has been with films made with a high proportion of water-soluble plasticizers.

On the evidence available, total kafirin- and commercial zein bioplastics are both similarly readily biodegradable under standard aerobic test conditions and have similar durability when used as in-tissue implants. This is notwithstanding the lower proteolytic digestibility of kafirin compared to zein (Emmambux & Taylor, 2009).

Overall, it can be concluded that, with the very notable exception of the gluten-water dough elastomer, kafirin and zein bioplastics have superior functionalities compared to gluten bioplastics. Furthermore, there are some differences in functional properties between total kafirin- and commercial zein bioplastic materials, with kafirin bioplastics having greater strength and less extensibility, and better moisture barrier properties. However, there is very little difference in functional properties between total kafirin and total zein bioplastics, with the exception of the higher stress recovery of total kafirin elastomers. Hence, the concept that because kafirin is more hydrophobic and less digestible, it produces superior bioplastics compared to zein requires qualification. Actually, it is that total kafirin bioplastics have generally superior functional properties compared to commercial zein bioplastics. Further, it seems that the greater degree of disulfide-bonded polymerization of the kafirin polypeptides is largely responsible for the differences in functional properties between kafirin bioplastics and zein bioplastics. Clearly, the extent of disulfide-bonded polymerization of different kafirin and zein preparations and its influence on their bioplastic functionality is a topic requiring in-depth study.

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