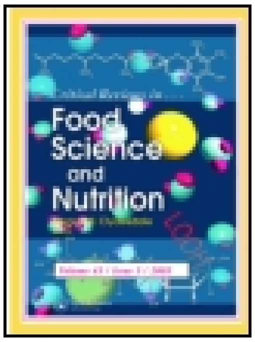


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Critical Reviews in Food Science and Nutrition

ISSN: 1040-8398 (Print) 1549-7852 (Online) Journal homepage: http://www.tandfonline.com/loi/bfsn20

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**To cite this article:** Tanushree Maity & Alok Saxena (2016): Use of Hydrocolloids as Cryoprotectant for Frozen Foods, Critical Reviews in Food Science and Nutrition, DOI: 10.1080/10408398.2016.1182892

**To link to this article:** http://dx.doi.org/10.1080/10408398.2016.1182892

Accepted author version posted online: 12 May 2016.

# USE OF HYDROCOLLOIDS AS CRYOPROTECTANT FOR FROZEN FOODS

TANUSHREE MAITY [1,*], and ALOK SAXENA [2]

[1]Defence Food Research Laboratory, Siddarthanagar, Mysore-570011, Karnataka, India

[2]Amity Institute of Food Technology, Amity University, Noida 210313, Uttar Pradesh, India

[*]Corresponding author E-mail: tanumft@gmail.com (Tanushree Maity)



## ABSTRACT

Freezing is one of the widely used preservation methods to preserve the quality of food products but it also results in deteriorative changes in textural properties of food which in turn affects its marketability. Different foodstuffs undergo different types of changes in texture, taste and overall acceptability upon freezing and subsequent frozen storage. Freezing and thawing of pre-cut or whole fruits and vegetables causes many deleterious effects including texture and drip losses. The major problem in stability of ice-cream is re-crystallization phenomena which happens due to temperature fluctuations during storage and finally impairs the quality of ice-cream. Frozen storage for longer periods causes rubbery texture in meat and fish products. To overcome these problems, hydrocolloids which are polysaccharides of high molecular weight, are used in numerous food applications involving gelling, thickening, stabilizing, emulsifying etc. They could improve the rheological and textural characteristics of food systems by changing the viscosity. They play a major role in retaining texture of fruits and vegetables after freezing. They provide thermodynamic stability to ice cream to control the process of re-crystallization. Hydrocolloids find application in frozen surimi, minced fish and meat products due to their water binding ability. They are also added to frozen bakery products to improve shelf-stability by retaining sufficient moisture and retarding staling. Various hydrocolloids impart different

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cryoprotective effects to food products depending upon their solubility, water holding capacity, rheological properties, and synergistic effect with other ingredients during freezing and frozen storage.

**Keywords**

Freezing, hydrocolloids, cryo-protectants, frozen storage

**INTRODUCTION**

Frozen foods form an important segment of processed foods due to their increased shelf-life and ability to retain flavor and fresh like characteristic without affecting the heat sensitive vital nutrients (Maity et al., 2011). The final quality of frozen foods depends on various factors such as size of the ice crystals formed, rapidity of freezing, and the type of material to be frozen (Fuchigami et al., 1994, 1997). Water inside the food freezes and expands to form ice crystals during the freezing process which causes the food matrix to rupture (Zounis et al., 2002). When this frozen food is thawed before consumption, the moisture readily separates from the food matrix and causes softening of the texture resulting in drip loss and often deterioration of the overall quality of the product (Rahman, 1999). The possible way to protect the food tissues from freezing damage is to control the structural integrity of food by controlling physico-chemical and thermo-mechanical properties of the freeze concentrated matrix surrounding the ice crystals in a frozen system (Lee et al., 2002). Rapid freezing mechanism and physico-chemical pre-conditioning of the food product could be helpful in retaining the overall quality in terms of texture (Bhattacharya et al., 2003). Hydrogen bonding and physical entrapment of water limits the formation of large ice crystals during freezing and frozen storage (Miyazawa, 2006). Cryo-stabilization is a process which describes the stabilization of frozen, freezer stored and freeze-dried foods (Seetapan et al., 2015; Levin and Slade, 1988). Cryo-stabilization protects quality of frozen food products, stored for longer durations at typical freezer temperatures from deleterious changes in texture due to solute crystallization, changes in structure due to shrinkage and collapse and changes in chemical composition due to oxidative rancidity and colour or flavour degradation (Levin and Slade, 1990).

Hydrocolloids are high molecular weight polymers (polysaccharides/ proteins) that could improve the rheological and textural characteristics of food systems and find wide applications in the food processing industry (Regand and Goff, 2002). Hydrocolloids are hydrophilic due to the presence of many hydroxyl groups in the structure and are polyelectrolyte. They are used in various food applications to provide adhesiveness, binding, bulk, cloud, as a gelling agent, foaming agent, emulsifier, film former, stabilizer and whipping agent (Bolliger et al. 2000). The main properties of hydrocolloids- gelling and thickening, comes from the viscosity producing effect when dispersed in water (Dickinson, 2003; Hinrichs et al., 2003). Hydrocolloids impart consistency and mouth feel to a variety of foods such as ice cream; puddings and crèmes; gels and gum confectionery; mayonnaise and dressings; beverages; meat products; instant foods; frozen ready meals (Scherz, 1997). Hydrocolloids are neutral in taste and flavor with minimal to none quantum of energy, which enables them to enter in any kind of food system without altering the acceptability (Nussinovitch, 1997). Natural hydrocolloids are a good source of soluble dietary fibers (up to 85% of dry mass), which reduces the concentration of cholesterol and improves gastrointestinal functions and glucose tolerance (Sozer, 2009). In addition, hydrocolloids serve as syneresis inhibitor in various frozen foods (Chaisawang and Suphantharika 2006). Many hydrocolloids are polyelectrolytes and have charged groups which ensure strong hydration. The presence of counter ions and co-ions cause complex behavior which may be ion-specific and depends on the concentrations of all ionic solutes (Vlachy, 2008). Alginate, carrageenan, carboxy methyl cellulose, gum Arabic, pectin and xanthan gum are some of the polyelectrolytes.

**Types of hydrocolloids**



 

Hydrocolloids can be obtained synthetically or isolated from vegetables, animals and microbial sources. Polysaccharides form a major group depending on the source for hydrocolloid applications. Hydrocolloids based on polypeptides such as gelatin also find various applications in food industry. Hydrocolloid polysaccharides may comprised of agar, algin, carrageenan which comes from seaweed; it may be tree exudates consisting gum arabic, gum karaya, gum tragacanth and gum ghatti; seed gums including locust bean and guar gum (Barak & Mudgil, 2014). Pectin and starches are some of the other polysaccharides used as hydrocolloids (May, 1990). Synthetic hydrocolloids are also derived from carbohydrates such as cellulose derivatives.

*Plant exudates*

Plant exudes viscous, gummy liquid which forms clear, glassy masses when exposed to air and allowed to dry. Gum arabic is obtained from various species of *Acacia* trees. Gum ghatti is amorphous exudate which is obtained from the tree of *Anogeissus latifolia*. Gum karaya is exuded from the *Sterculia urens* tree. The very old gum tragacanth is an exudate of plants of *Astragalus genus*.

*Plant seed gums*

Most common plant seed gums used as hydrocolloids are locust bean gum which is obtained from leguminous plant *Ceratonia siliqua* L. and guar gum, which is derived from seeds of *Cyamopsis tetragonolobus* plants (Barak and Mudgil, 2014). Other gums of least commercial application in food are psyllium seed gum from *Plantago psyllium* and quince seed hydrocolloid which comes from *Cydonia vulgaris* tree. They are polymers of sugars other than starch which is stored in the seeds. The glucose polymers consist of galactose and mannose.

*Pectin*

Pectin is a complex heterogeneous structure composed of polygalacturonide chains with varying molecular weights (Thakur *et al.*, 1997). Pectic substances are an integral part of cellular structure which serves to cement the middle lamella. It is the most common hydrocolloid used in canning and confectionery industry because of its simplicity of gelatinization in low acidity and in high soluble solids content conditions (Basu and Shivhare, 2010).

*Seaweed extracts*

Hydrocolloids such as carrageenan, agar, and alginate commercially used in various food applications, are extracted from seaweed. Carrageenan and agar are obtained from a group of red algae (*Rhodophyceae*) and alginate is extracted from brown algae (*Phyophyceae*).

*Starches*

Starch is a very important natural bio-polymer which finds diverse applications in food and polymer industries. Adebowale and Lawal (2002) reported that the application of starch to improve the texture of food is primarily governed by its unique property of gelation, gelatinisation, pasting, solubility, swelling, colour and digestibility. It is mainly used as a thickener, colloidal stabilizer, gelling agent, bulking agent, water retention agent and as an adhesive. The unique functional characteristics imparted by starches in various food applications vary with its biological origin (Singh et al., 2003). Starches display much of its functionality due to the physical organization of two major high-molecular-weight carbohydrates, amylose and amylopectin, into the granular structure (Faria-Tischer et al. 2006). The most significant sources of starch are cereal grains and tubers such as corn, wheat, rice, potato and cassava (Betancur-Ancona et al., 2001). Starches from cereal origin as well as from fruits and vegetables, have received extensive attention in relation to structural and physico-chemical properties in the recent years. Non-conventional starches have progressively been gaining importance because of their potential application in the development of new products or improvements in functional uses. Non-conventional starches could offer a broad range of potential industrial use due to their diverse physicochemical, structural and functional characteristics. Several researchers are engaged in identifying and isolating starches from non-conventional sources such as from banana (Wang et al., 2014), makal (Torruco-Uco and Betancur-Ancona, 2007), cocoyam (Falade and Okafor, 2013), innala tuber (Jayakody et al., 2005). The most common hydrocolloids, their properties and uses in various food applications are listed in Table 1. Fully cooked or partially precooked frozen foods containing sauces, gravies, pie fillings or desserts undergo undesirable changes after the freezing process which may reduce consumer acceptability. Starches as a cryoprotecting agents play a crucial role in stabilizing the structure and texture of frozen foods (Sim et al., 2011). Their distinctive thickening power and interaction with other stabilizers enable to preserve the original characters of frozen foods.

*Modified starches*

Starch modification has brought out numerous possibilities to improve product quality by decreasing retrogradation, gelling tendencies of pastes and gel syneresis of native starches (Choi & Kerr, 2003). Starches can be modified by chemical, physical and enzymatic treatments. Chemical treatment involves derivatization such as etherification, esterification, cross-linking and grafting of starch. Chemical modification introduces functional groups into the native starch molecule, resulting in altered physico-chemical properties. Physical method of starch modification involves acid hydrolysis and oxidization of starch or treatment of starch using heat or moisture. Modifications of starch through enzymes involve hydrolysis (Singh et al., 2007).

These modifications improve paste clarity and sheen, paste and gel texture, film formation and adhesion. Modified forms of starches impart better freeze-thaw and cold storage stabilities than the native counterparts (Shi and BeMiller, 2000). Syneresis is a common phenomena observed in frozen fruits and vegetables during thawing. Modified starches have been used extensively to reduce the deteriorative effects of freezing on plant tissues.

*Gelatin*

Gelatin is a high molecular weight water soluble proteinaceous hydrocolloid which serves multiple functions with a wide range of applications. Gelatin is obtained by the thermal denaturation and partial hydrolysis of collagen derived from the skin, white connective tissue and bones of animals by destruction of the tertiary, secondary and to some extent the primary structure of native collagens (Fernandez-Diaz et al. 2001). It finds its uses in a wide range of food products due to its gelling and thickening properties. The main functional properties of gelatin are associated with gelling (gel strength, gelling time, setting and melting temperatures, viscosity, thickening, texturizing, and water binding) and the surface behaviour (emulsion formation and stabilization, protective colloid function, foam formation and stabilization, film formation, and adhesion/cohesion (Schrieber and Gareis, 2007). The strength, viscosity, setting behaviour of gel and melting point of gelatin depends on the molecular weight distribution and on the amino acid composition (Karim and Bhat, 2008).

**Functional properties of hydrocolloids**

In processed food products hydrocolloids are added to impart desirable textural and functional properties. Hydrocolloid influence the processing conditions by retaining water, reducing evaporation rate, modifying ice crystal formation and participating in chemical reactions

(Linlaud et al., 2011). They have a wide range of specific food applications such as adhesive, binding agent, bulking agent, crystallization inhibitor, clarifying agent, emulsifier, encapsulating agent, foam stabilizer, gelling agent, swelling agent, syneresis inhibitor, thickening agent and whipping agent (Matuda et al., 2008). The general function of hydrocolloids can be defined in terms of the following major properties.

*Thickening*

Hydrocolloids disperse in water to give a thickening or viscosity producing effect. The degree of thickening varies with the type, nature and concentration of hydrocolloids. Most of the hydrocolloids give high viscosities at concentration less than 1%, very few of them give low viscosities at a fairly high concentration (Glicksman, 1982). The process of thickening involves the non-specific entanglement of conformationally disordered polymer chains; it is essentially a polymer-solvent interaction. The thickening effect of the hydrocolloids not only depends on the concentration and type of hydrocolloid used but also, on the pH, temperature and type of the food system (Ribotta et al., 2004). Hydrocolloids such as are starch, xanthan, guar gum, locust bean gum, gum karaya, gum tragacanth, gum Arabic and cellulose derivatives are used as thickeners (Saha and Bhattacharya, 2010).

*Gelling*

Hydrocolloids become viscoelastic in nature when added to water forming gels which exhibits both characteristics of a liquid and a solid (Rosell et al., 2001). Gel formation involves association or cross-linking of the polymer chains to form a three dimensional network that traps or immobilises the water within it to form a rigid structure that is resistant to flow. Hydrocolloid gels are often referred to as physical gels as they form gels by physical association of their polymer chains through hydrogen bonding, hydrophobic association and cation mediated cross-linking. They differ from synthetic polymer gels which normally consist of covalently cross-linked polymer chains (Philips and Williams 2000). The important gelling type hydrocolloids that find application in foods include alginate, pectin, carrageenan, gellan, gelatin, agar, modified starch, methyl cellulose and hydroxypropylmethyl cellulose.

*Emulsifiers & emulsion stabilizers*

Most of the hydrocolloids act as stabilizing agents of oil-in-water emulsions. However, a few hydrocolloids exhibit surface activity at the oil–water interface and can act as emulsifying agents by assisting in the formation and stabilization of fine droplets during and after emulsification (Sim et al., 2011). Hydrocolloids used as emulsifiers in food applications are gum arabic, modified starches, modified celluloses, pectin and some galactomannans. The emulsifying property of hydrocolloids is due to the non-polar chemical groups attached to the hydrophilic structure or the presence of a protein component linked covalently or physically to the hydrocolloid (Dickinson, 2004; 2009). Hydrocolloids stabilises the emulsion by slowing down or even preventing the creaming process by modifying the rheology of the continuous phase, in conjunction with 'weighting agents' to match the densities of oil and aqueous phases (Taherian et al., 2008). Thickening effect of hydrocolloids increases the viscosity of the aqueous phase so that it slightly exceeds that of the oil and reduces the tendency of the dispersed phase to coalesce. Hydrocolloid has destabilizing effect on the emulsion at very low concentrations as the non-adsorbing hydrocolloid induces the depletion flocculation which causes enhanced serum separation of the emulsion. However, at higher hydrocolloid concentrations, the viscoelastic character of the interconnected regions of emulsion droplets inhibits creaming (Dickinson, 2009). Hydrocolloid stabilizers are used to prepare stable emulsion in ice cream, sherbets and frozen desserts.

**Role of hydrocolloids in frozen fruits and vegetables and their products**

The most detrimental effect of freezing is physical disruption to cell or cell components of plant tissues (Upadhyay et al., 2012). Freezing involves freezing of water present in the plant tissue. The ice crystal begins to form from the water present in the extra-cellular medium and progresses via the cytoplasm which cause the cell membrane to loose its permeability. After freezing and thawing, texture of fruits and vegetables becomes soggy as the cell wall breaks down and the moisture separates from the cellular matrix, causing softening of the tissues, syneresis, and deterioration of the overall quality (Alonso et al., 1997; Jul, 1984). The freeze-induced damage of cell membrane results in loss of fresh-like characteristics of the product, turgor loss and the consequent loss of cell viability. Several attempts have been made to improve the resistance of fruit and vegetable tissues to freezing damage (Moraga et al., 2006; Suutarinen et al., 2000). Maintenance of texture and physical stability of the plant materials having relatively high moisture contents is very critical and receives control of water binding by using hydro-dynamically active ingredients such as hydrocolloids. Incorporation of compounds which can bind the water to offer protection against the deleterious effects of freezing and thawing have been described by several researchers (Lee et al., 2002; Park et al., 2006).

Maity et al. (2011) studied that hydrocolloid pre-conditioning of the pre-cut carrot could be helpful in retaining the quality after freezing and thawing. They reported the effectiveness of different hydrocolloids such as CMC, Xanthan gum, alginate and pectin in controlling the detrimental effect of freezing. Xanthan gum (0.4%) was adequately found to reduce the textural losses due to freezing in pre-cut frozen carrot. Their results were also supported by the thermodynamic studies for glass transition which indicated suitability of hydrocolloids in decreasing the glass transition temperature. Hydrocolloid pre-treatment has also been found suitable in retaining the cellular structure of melons after freezing (Resende and Cal, 2002). Tissue disruption to freezing was reported to be less in melon pieces coated with pectin solution. Authors suggested the interaction of hydrocolloid system with the melon cell wall for decrease in damage of the fruit structure. Hydrocolloids not only prevent the fruit and vegetable tissue for being disrupted during freezing process but also maintain the sensory and textural quality during long term frozen storage. Maity et al. (2013) reported usefulness of hydrocolloids such as pectin, carboxy-methyl cellulose, xanthan gum and alginate in retaining the texture and sensory acceptability of pre-cut carrots during frozen storage. Pectin is also found to act as a retrogradation and syneresis inhibitor in tapioca starch-pectin mixture model during freezing (Agudelo et al., 2014).

Mixture of certain cryoprotectants could improve the deleterious effects of freezing and thawing on the sensory and physical properties of cooked mashed potatoes. Downey (2002) worked on cryoprotective effects of hydrocolloids on cooked carrot, potatoes and turnips after freezing and thawing and reported that addition of xanthan gum and guar gum in cooked vegetables were more effective in reducing the drip losses than carrageenan and pectin without affecting the appearance and colour of the product. However, selection of appropriate cryoprotectant for quality maintenance was found dependent on the type of vegetables used. In another study, Downey (2003) described two types of cryoprotectant mixture, first consisting of guar, pectin and whey protein concentrate and another consisting of xanthan, carrageenan and sodium caseinate. He concluded that both the mixtures reduced the maximum resistance to penetration and centrifugal drip loss.

Mashed potatoes are an ideal material suitable for freezing as they can either be used as a ready-meal component or as a single product. It has been reported to be stabilized for long-term frozen storage by many researchers using cryo-protectants mixtures of various hydrocolloids such as amidated low-methoxyl pectin, kappa-carrageenan and xanthan gum and sodium caseinate and xanthan gum (Fernandez et al., 2009). This combination of kappa carrageenan and xanthan gum was found to retain the texture and water holding capacity for 1 year of frozen storage. The sensory acceptability of mashed potato after 1 year of frozen storage was found to be maintained when two different combinations of hydrocolloids were used i.e. kappa-carrageenan-xanthan gum and sodium casienate-xanthan gum. In agreement with these results, Bikaki et al. (2013) also reported sensory flavour and texture retention in frozen mashed potatoes as effect of addition of different hydrocolloids. Alvarez et al. (2008) also investigated cryoprotective effects of hydrocolloids in improving the mechanical properties, color and sensory properties of frozen/ thawed mashed potatoes. They reported that the dairy proteins affected the taste undesirably and xanthan gum was preferred for better sensory attributes compared to the other hydrocolloids. Alvarez et al. (2009) suggested low concentration of kappa carrageenan and xanthan gum addition to frozen thawed mashed potato on the basis of overall acceptability. Kappa carrageenan was reported to provide the appropriate texture, while xanthan gum imparted creaminess to the product, which was associated with an increase in the amount of xanthan gum–water interactions and reduced starch retrogradation. Cryoprotectants could also improve the rheological properties of frozen/ thawed mashed potatoes (Alvarez et al., 2010). Addition of cryoprotectants not only resulted in better water holding capacity but also the improved visco-elastic behaviour of frozen/ thawed mashed potatoes. Hydrocolloids have also been found to reduce drip losses in frozen curries consisting vegetables as predominant component in gravy which are highly prone to liquid separation and textural losses after thawing (Maity et al. 2012).

Use of higher concentration of pectin as a pre-treatment could successful retains the cellular fluid loss, texture and solution viscosity of strawberries after freezing and thawing (Reno et al. 2011). The effect could be increased if used along with vacuum impregnation as it was recorded when pectin pre-treatment in combination with sugar and $CaCl_2$ could effectively prevent freezing losses in strawberries as well as retained phyto-chemicals. Pectin alone was found to retain anthocyanin in range of 3.0 to 25.1 % (Oszmianski et al., 2009). Mushroom being a highly delicate and soft tissue is prone to textural losses during freezing and thawing Pre-freezing treatment with low methylated pectin could also protect the texture of mushroom after freezing. Garcia-Berbari et al. (1998) also used pectin (0.5%) in pre-freezing treatment of strawberries for retention of quality after frozen storage. Nunes-Fernandes et al. (2010) established a faster thawing process of the strawberry pulp added with sugar and pectin. The synergistic effect of sugar and pectin increased the freezing velocity of the pulp. Cryoprotectant effect of sucrose solutions on retention of mechanical properties of kiwifruit, mango and strawberry was found to be significant due to freezing and thawing as reported by Chiralt et al. (2001).

**Role of hydrocolloids in frozen dairy products**

Hydrocolloids maintain homogeneity in the ice-cream and control ice crystal growth during the freezing/ aeration process by reducing the amount of free water by immobilizing it within the gel structure (Keeney, 1982). During serving and consumption, hydrocolloids contribute to uniform melt down, mouth feel and texture of ice cream. According to Goff (1997), a stabilized ice cream resists structural changes in a dynamic environment. Hydrocolloids affect the physical and sensory properties of dairy desserts. Application of hydrocolloid in ice cream increases stiffness; enhances whipping during aeration; prevents lactose crystallization; prevents shrinkage during storage; stabilizes the emulsion; and contributes to body, texture and creaminess. Hydrocolloids play a crucial role in resisting the structural changes due to 'heat shock' which occurs due to the inevitable temperature fluctuations during storage and distribution that creates ice crystal growth and other types of deterioration, leading to structural changes.



Hydrocolloids are added in ice-creams or frozen desserts not only to produce a smooth texture but also to retain the same during frozen storage. Three mechanisms describe the cryoprotective effect of hydrocolloids on ice cream; the first mechanism describes increase in viscosity of ice cream which is correlated to the control of ice crystal growth (Hagiwara and Hartel, 1996). The second mechanism correlates the cryo-protectivity of hydrocolloids with their ability to form cryo gels as a result of temperature fluctuations during storage (Blond, 1988; Muhr and Blanshard, 1986). The third mechanism suggests that the incompatibility of hydrocolloids with proteins aggravate phase separation and retard re-crystallization (Regand and Goff, 2002, 2003). Bolliger et al. (2000) reported that the freeze concentration of hydrocolloids in the serum phase of ice cream is responsible for the rheological changes in ice-cream which contributes to the efficient control of water. However, earlier, Miller-Livney and Hartel (1997) reported that the changes in macro-viscosity caused by addition of hydrocolloids are associated with the micro-viscosity changes which may retard the diffusion of unfrozen water to the ice crystals.

The glass transition temperature ($Tg$) and crystallization of amorphous components affects the physical state of a system. Increasing the effective molecular weight in the amorphous phase of frozen saccharide system increases the *Tg*. The physical state of an amorphous matrix in a frozen food system greatly influences the stability, since it effect the chemical and physical changes during processing and storage. Hence, the glass transition temperature is a marker that can determine the stability of frozen systems (Roos and Karel, 1991). If *Tg* is greater than freezer temperatures the frozen food will experience minimal deterioration. Dextran may be useful as a cryostabilizing agent in frozen dairy products as it could increase the effective molecular weight while not being limited by excessive viscosities that would impose pumping constraints (McCurdy *et al.*, 1994).

Fernandez et al. (2007) applied high pressure freezing along with addition of hydrocolloid in sucrose solution (16% w/w) to analyze the ice crystal formation. They found smaller ice crystals in sucrose solution added with a mixture of locust bean gum and xanthan gum, irrespective of the freezing method employed. Hydrocolloids also influence the textural quality, control the flavor intensity, improve the perceived creaminess and affect the melting characteristics of frozen dairy desserts (Soukoulis *et al.*, 2008). The use of xanthan gum or hydroxyl propyl methyl cellulose at a level of 0.3 g/ 100 g in full fat (4 g/100 g milk fat) and low acidified (25 g/ 100 g yoghurt addition) formulations has been recommended to achieve improved creamy sensation, high textural quality and enhanced flavor in ice-cream (Soukoulis et al., 2010).

Most commonly used hydrocolloids in ice-cream are polysaccharides such as CMC, pectin, locust bean gum, hydroxyl ethyl starches and guar gum (Garcia-Ochoa *et al.* 2000). Locust bean gum has been reported to cause highest viscosity in the ice cream and lowest overrun (Sung et al. 2006). In the same study, pectin was reported to decrease the ice crystal size significantly in the ice cream mixes as compared to gelatin, locust bean gum and hydroxyl ethyl starches addition. Better melt resistance and increased melting time was the advantages reported by the authors. Patmore et al. (2003) investigated the cryo-gelatin properties of locust bean gum and guar gum in ice cream model systems. Locust bean gum was found to form weaker gels on temperature cycling in combination with MSNF. Also fat droplets inhibited the formation of locust bean gum gels. Their study confirmed that fat emulsions behave differently to locust bean gum containing solutions. Hydrocolloids have also been used to stabilize frozen yoghurt. Weon and Sun (1996) reported that incorporation of low methoxy pectin (LMP) resulted in sandy and icy yoghurt while propylene glycol resulted in chewy and soft textured yoghurt. Soukoulis et al. (2008) evaluated functionality of various primary hydrocolloids such as CMC, guar gum, sodium alginate and xanthan gum along with kappa carrageenan which was used as a secondary stabilizer in the ice cream mix. Their study indicated that use of these hydrocolloids could beneficially affect the textural quality of ice cream during storage. The addition of kappa-carrageenan as a secondary stabilizer proved to be a crucial factor for the cryo-protection. A combination of high pressure processing along with different hydrocolloids in the ice cream mix was found to be effective in enhancing the quality of ice cream. High pressure shift freezing achieved smaller ice crystals than the high pressure assisted freezing. They also concluded that smaller ice crystals were attained when mixture of locust bean gum and xanthan gum were added to the sucrose solution irrespective of the freezing method. Lots of studies have been conducted to evaluate the efficacy of hydrocolloids to stabilize frozen yogurt. Shin and Yoon (1996) reported propylene glycol added frozen yogurt very soft in texture. However, addition of locust bean gum was reported to result in a coarse, icy, crumbly and sandy texture in frozen yogurt.

**Role of hydrocolloids in frozen animal food formulations**

Freezing and frozen storage are important techniques for long-term preservation of animal products such as surimi, processed meat and fish muscle preparations. However, freezing generally result in a loss of protein functionality by damaging muscle protein and inducing protein denaturation. This causes losses in water holding capacity of the animal tissue and development of rubbery texture which affect sensory acceptability as well as marketability (Herrera and Sampedro, 2002; Park and Morrissey, 2000; Okada, 1992). Fish muscle proteins denatures due to freezing in the order of decreasing solubility of myofibrillar proteins, disappearance of ATP-induced contraction of muscle fibers, and lowering of myosin ATPase activity (Suzuki, 1981). Polyols have been extensively used as a cryoprotectant in frozen animal food preparations (Sych et al., 1990, Park et al., 1996, Jasra et al., 2006). Sultanbawa and Chan (1998) suggested effectiveness of sugar and polyol such as sorbitol, lactitol blends as cryoprotectants in ling cod surimi during frozen storage. Uijttenboogaart et al. (1993) also studied the effectiveness of polyols and high molecular weight carbohydrates for stabilization of chicken myofibrillar protein isolates during frozen storage. They found that 2.8 % sorbitol along with 4 % starch could be an effective combination in maintaining the product integrity. Sugars and sugar alcohols have also been reported to be used for stabilization of adriatic pilchard surimi (Kovacevic and Kurtanjek, 1997). Chen et al. (1991) found stability in chicken surimi during cold storage (-18 °C) added with 1:1 (w/w) sucrose/ sorbitol mixture for 2 months. The protein denaturation induced by freezing was found to be reduced when sorbitol, glucose syrup, sucrose and sucrose/ sorbitol (1:1, w/w) mixture was added at 8% (w/w) in cod-surimi (Sych et al., 1990). Goeller et al. (2004) optimized level of sorbitol into intact fish muscle and monitored the cryoprotection during freezing and thawing as change in myosin $Ca^{2+}$ ATPase activity. Authors reported that excellent cryoprotection was found when 60% sorbitol was incorporated into intact fish muscle during freezing.

Undesirable deteriorative changes, such as changes in odour, colour, flavour, and texture of surimi continues to occur during frozen storage (Osako et al., 2005). Cryoprotectants, such as sorbitol, sucrose, and polyphosphates, are normally added to the surimi during processing to ensure the maximum protein quality during frozen storage (Etemadian et al., 2011). Mostly, these commercial cryoprotectants are chosen because of their relatively low cost, wide availability, and excellent cryoprotective effects. A mixture of sorbitol and sucrose can also be used as a freezing point regulator. The freezing point of common carp surimi can be decreased from -1 to -3 °C by the addition of a 4% commercial cryoprotectant blend (sucrose: sorbitol, 1:1) (He et al., 2012). However, Liu et al. (2014) reported that the super-chilling of Carp surimi at 3 °C with added cryoprotectants (mixture of sugar and sorbitol) inhibited lipid oxidation, reduced the TVB-N, improved the microstructure, maintained good quality and low microbiological counts throughout the storage period,. Cryoprotectants were also found to be very effective in preventing surimi quality deterioration by lowering water activity ($a_w$), decreasing protein freeze denaturation, and reducing ice crystal mechanical damages during super chilling storage.

A quantity as low as 1% modified tapioca starch could also reduce the breaking force, deformation and expressible moisture content of bigeye snapper mince gels subjected to different freeze-thaw cycles (Tuankriangkrai and Benjakul, 2010). Malto-dextrins used at 8% in Alaska Pollock Surimi were found to protect the surimi against freeze-thaw stress (Carvajal and Lanier, 1996). Divalent cation such as zinc was found to enhance the effectiveness of cryoprotectants for stabilizing fish acto-mysin during freezing (MacDonald et al., 1996). Cellulose in powder form has been found to stabilize the surimi based shellfish analogue products by modifying the texture. Cellulose at 2% concentration can be used in place of conventional cryoprotectants (4% sorbitol and 4 % sucrose) for stabilizing the surimi against freeze-thaw stress (Yoon and Lee, 1990). In a study to stabilize the protein and unfrozen water of lizardfish surimi, Somjit et al. (2005) found that shrimp chitin hydrolysate suppressed the freeze induced denaturation by stabilizing water molecules that surrounds the protein. They also reported that shrimp chitin has no cryoprotective effect on stabilization of protein during freezing. Cryoprotective effects of different form of oligosaccharides such as fruto, isomalto and galacto-oligosaccharides on beef protein after 7 freeze-thaw cycles has been proven by Lee et al. (2001). The oligosaccharides were also found to retain mechanical properties of surimi stored at -18 °C for 3 months (Auh et al., 1999). Telis and Kieckbusch (1998) reported that sucrose, glycerol and magnesium chloride improved cryoprotectant effect by preventing egg yolk gelation during freezing. However salt of calcium (calcium chloride) promoted protein coagulation before freezing. Gum Arabic and kappa carrageenan were found to be the best cryo-protectants for storage of beef at -18 °C (Akkose and Aktas, 2008).

Thermal analytical techniques such as differential scanning calorimetry (DSC) and Differential Thermal Analysis (DTA) have been extensively used to study the cryoprotective effects of various hydrocolloids. Kovacevic et al. (2011) used thermal analytical techniques to prove the cryoprotective effects of polydextrose on chicken surimi. They reported that highest level of polydextrose (10%) exhibited greatest cryoscopic depression of initial freezing point ($T_i$) and increase in thermal transition temperature ($T_p$). The cryoprotective effect of polydextrose was confirmed from higher values of denaturation enthalpy ($\Delta$H). Similarly DSC studies were made to study the cryoprotective effect of kappa carrageenan on chicken surimi during rapid freezing. The higher value of $\Delta$H indicated higher cryoprotective effect of kappa-carrageenan and lesser damage to native proteins (Kovacevic et al., 2009). Contribution of polysaccharide to stability in frozen dairy products could be accredited to the fact that the influence of these stabilizers on ice crystal size above the glass transition temperature is a function of the kinetic properties of the freeze-concentrated, visco-elastic liquid surrounding the ice crystals (Goff et al., 1993).

**Role of hydrocolloids in frozen dough and baked products**

Freezing and frozen storage efficiently slow down the staling of baked products especially bread (Rodge et al., 2012). However, frozen dough affects the further bread making quality by affecting the micro-structure and baking performance of the dough. Freezing of dough influences the physical properties of final baked breads which lead to its unacceptance. During frozen storage, the gluten network, glutelin and gliadin components of the dough are depolymerised which causes a final bread volume reduction (Havet et al., 2000; Ribotta et al., 2001). The final quality of bread baked from frozen dough also deteriorates if the storage temperature is not maintained below sub-zero temperature (Selomulyo and Zhou, 2007). The cryoprotective effect of hydrocolloids from freezing in baked food products has been demonstrated by several researchers. Hydrocolloids acts as dough improvers and are normally added to bakery products to improve shelf-stability by retaining more moisture and retarding staling as they have the ability to induce structural changes in the main components of dough (Twillman and white, 1988). Hydrocolloids mixture of hydroxypropylmethyl cellulose, xanthan gum, guar gum could be used to improve the rheological and textural properties of gluten free dough for the preparation of empanadas and pie crusts. Hydrocolloid functions in multiple ways to improve the quality of baked products. Different hydrocolloids impart different functionality depending on their individual functional properties such as solubility, gelling power, rheological properties and synergistic effect with other ingredients. The amount of hydrocolloid used also influences the bread quality. 0.1 % hydroxypropyl methyl cellulose (HPMC) was reported as a promising anti-staling agent in frozen-stored bread, reducing both the dehydration rate and the crumb bread hardness (Barcenas et al., 2004). Other hydrocolloids such as xanthan gum, locust bean gum and guar gum acts as texture improvers. They control the moisture retention and induce gas retention in dough, resulting into increased yield of baked products (Collar et al., 1999; Guarda et al., 2004; Mandala et al., 2007; Mandala and Sotirakoglou, 2005; Mettler and Seibel, 1993). Hydrocolloid addition in formulations was reported to increase the quality of hot press wheat tortillas (Friend et al., 1993). Increased levels of hydrocolloids resulted in less cohesive tortilla dough. CMC in the dough was found to retain the rollability of tortillas longer after five freeze-thaw cycles. Final quality of defrozen bread has been improved by modifying formulations focusing effect on gluten (Miller et al., 2003; Ozmutlu et al., 2001). Interaction of different ingredients with hydrocolloids including emulsifiers has also been studied to improve the frozen bread quality (Clarke and Farrell, 2000). Xanthan gum is reported to improve the freeze-thaw stability in starch-thickened frozen foods (Rosell et al., 2001; Sanderson, 1981). Xanthan addition has been found to induce dough strengthening due to a strong interaction with the flour proteins which increases water absorption capacity and the ability of the dough to retain gas, the specific volume of the final bread and the $a_w$ of the crumb (Collar et al., 1999; Rosell et al., 2001).



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Mandala et al. (2008) studied the effect of hydrocolloids namely, xanthan gum, guar gum, hydroxyl propyl methyl cellulose and locust bean gum on the physical properties of bread dough, semi-baked bread and fully baked breads after frozen storage of one week. Final bread characteristics were reported to be improved due to the addition of hydrocolloid which were more pronounced in bread dough and semi-baked bread. Xanthan gum and locust bean gum rich doughs were found to be the most stable in terms of changes in strength and dough extensibility during storage. Freezing of partly baked bread could also result in higher sensory and textural quality, close to those of fresh in final baked bread (Fik and Surowka, 2002). Barcenas et al. (2003) evaluated that the crumb hardness of full baked breads after freezing of partially-baked breads increased with the time of frozen storage. They suggested that the addition of hydrocolloids in the bread making process retarded the staling of bread by decreasing the retrogradation enthalpy of the amylopectin after the full-baking of partialy -baked frozen stored breads. Freezing of fully baked food products instead of the dough has been found more efficient, avoiding the problem of yeast damage. But, the quality of de-frozen breads depends on baking conditions, storage and re-baking parameters (Leuschner et al., 1997, 1999).

Microwave heating is very common and popular for thawing frozen baked products. However, frozen bakery products reheated (thawed) in a microwave oven may develop undesirable characteristics such as low bulk volume, less surface browning, flavor development, non homogeneous heating, tough and rubbery texture and difficulty to chew crumb. Rapid staling after heating in microwave could be accredited to mainly due to re-crystallisation of starch (Rosenberg and Beogl, 1987; Shukla, 1993; Yamauchi et al., 1993; Yin and Walker, 1995; Pan and CastellPerez, 1997). Hydrocolloids such as xanthan and guar gum are effective in improving bread quality not only during frozen storage but also during re-heating (thawing) process under microwave. This may be due to the fact that in the microwave thawing process, an increased water holding capacity in baked product is desirable which hinders a rapid water loss and result in less toughening, which could be achieved by using hydrocolloids in the formulations.

Guar gum has also been used in frozen baked foods due to its thickening, stabilization and water-binding properties. It improves mixing tolerance and product shelf-life through moisture retention and prevents syneresis in frozen foods and pie fillings (Maier et al., 1993). Similarly, Rasanen (1998) reported that addition of hydrocolloid could minimize the amount of liquid phase due to ice crystal growth in dough during frozen storage. Ribotta et al. (2004) also reported similar observation in final bread baked from frozen dough added with DATEM emulsifier and guar gum as additives to prevent the negative effect of frozen storage on micro-structural and dynamic rheology of the dough. Addition of natural gums as hydrocolloids were found to improve the water absorption of the tortilla dough and resulted in more round, puffed and good quality tortillas (Friend et al., 1993). The use of CMC has been reported to retain roll ability of these tortillas after 5 freeze-thaw cycles. Effect of water and hydrocolloids on staling of white bread has been reported by Davidou et al. (1996). The authors found that the firmness and rate of increase of firmness during storage were reduced due to hydrocolloid addition to breads.

Cereal products based on gluten are not suitable for celiac people. Hence, replacement of gluten with other network forming components such as hydrocolloids in dough formulation without gluten has been researched extensively in the past few years. Lorenzo et al. (2009) evaluated the effect of hydroxy propyl methyl cellulose and mixture of xanthan/ guar and xanthan/ hydroxyl propyl methyl cellulose on the rheological properties of refrigerated and frozen non-fermented gluten free dough. It was revealed that xanthan/ HPMC dough was preferred over the commercial dough. The improved textural characteristics of dough were accredited to the formation of continuous matrix by hydrocolloid entanglements. Hydrocolloids were also found applicable as cryopropective in batter systems. Methylcellulose incorporated in to batter for preparing a frozen battered food without a pre-frying stage has been reported by Sanz et al. (2004). Squid rings treated with 1.5 and 2 % methyl cellulose in the batter could be immersed in a 70-80 °C water bath and subsequent thermal processing sets the gel structure prior to freezing.

Loaf volume of bread acts as an indicator of quality changes in case of frozen dough as the freezing process followed by frozen storage affects the gassing power of yeast (El-Hady et al., 1996; Sharadanant & Khan, 2003). An increase in dough proofing time and reduction in specific loaf volume is very common in frozen doughs and the negative effects of frozen storage are more prevalent at longer duration of storage (Berglund et al., 1991). Decrease in loaf volume during frozen storage is due to ice recrystallization, which in turn causes loss in yeast viability and damage to the dough gluten and starch network to retain $CO_2$ (Lorenz and Kulp, 1995). Damage of starch during frozen storage contributes to increased moisture retention resulting in increased loaf weight and lower loaf volume (Berglund 1988).

Hydrocolloids acts as cryoprotectants by providing stability to starch-based products during freeze–thaw cycles and minimize the negative effects of freezing and frozen storage (Liehr and Kulicke, 1996). Hydrocolloids and starch interact with each other to form starch polymer complexes (Bahnassey and Breene, 1994). Hydrocolloids affect the physical, pasting, rheological and thermal properties of starch and dough such as melting, gelatinization, fragmentation and retrogradation (Fanta and Christianson, 1996; Rojas et al., 1999). Increased specific loaf volumes of breads by adding hydrocolloids compared to control has been reported by several researchers. Mandala (2005) described the increase in specific loaf volume of bread made from frozen dough added with xanthan gum (0.16% flour basis). Table 2 shows the specific loaf volumes of bread loaves with and without the hydrocolloids indicated that the addition of hydrocolloids improved the quality of frozen dough. The difference in the functional performance of frozen dough and the subsequent specific loaf volumes of bread not only depends on the nature, origin and dosage of the hydrocolloids incorporated into the dough, but also, on the formulation and processing conditions (Selomulyo and Zhou, 2006). It should be noted, that the addition of k-carrageenan (0.5 %) in the formulation affected the specific volume of final bread made from the frozen dough after storage for 42 days, negatively (Barcenas et al., 2004). The decrease in specific volume is due to the formation of rigid gels by the k-carrageenan sample that are not stable to freeze–thawing cycles (Gurkin, 2002; Ward & Andon, 2002).

Expulsion of water (syneresis) from a freeze–thaw gel is an important parameter to evaluate the ability of gel to withstand the detrimental changes which occur due to freezing and subsequent thawing. Syneresis is caused by thermal energy fluctuation and phase change of water during freezing and thawing. The amount of water released from the gel structure has also been reported due to increase in starch molecular associations resulting in retrogradation of amylose (Morris, 1990; Karim, Norziah, & Seow, 2000). Hence, it is also used as an indicator of the tendency of starch to retrograde. The ice crystals disrupt the gel matrix of starch during freezing and upon thawing it is released as bulk phase water from the polymeric network which leaves the starch gel into a spongy mass (Ferrero et al., 1994).

**Role of hydrocolloids in whey and sucrose model systems**

Hydrocolloids have been used in the sucrose or whey based solutions to control ice re-crystallization upon freezing and storage. In a study on whey model solutions, Herceg et al. (2000) reported that the CMC based hydrocolloids, freezing process and solution composition affect the fluidity of the solution. The viscosity was reduced in the hydrocolloid-whey solution than the hydrocolloid-water solution due to the interaction between hydrocolloid and whey proteins or minerals. Goff et al. (1999) investigated that locust bean gum forms a gel like network in sucrose solution and sucrose with skim milk powder solution. They reported that locust bean gum was effective at inhibiting re-crystallization than guar gum. However, carrageenan was reported to increase the rate of re-crystallization. Cryo-protective effects of hydrocolloids in a starch-sucrose-hydrocolloid system were also reported by Ferrero and Zaritzky (2000). Addition of hydrocolloids such as xanthan gum, guar gum and sodium alginate minimizes the structural damage by inhibiting formation of a spongy matrix resulting from amylopectin retrogradation without affecting the gelatinization temperature of the corn-starch-sucrose system. Overall, the introduction of hydrocolloids into the system was found to maintain acceptable texture during frozen storage at -18 ºC. Freezing is found to have no effects on viscosities of modal solution containing sucrose, sorbitol and lactose as effect of addition of carboxy methyl cellulose. However, the viscosity increased in whey based modal solutions confirming the significant effect of composition of modal solution, type of carboxy methyl cellulose and the freezing process on rheological parameters (Hegedusic et al. 2000).

**Role of hydrocolloids in frozen starch gels**

Retrogradation and syneresis are the common phenomenon in frozen starch gels or pastes because the water could be easily expressed from the dense starch network (Karim et al., 2000).

In the freezing process, phase separation occurs in starch pastes or gels due to the formation of ice crystals. Phase separation further increases in the thawing process as these starch pastes or gels results in a starch-deficient aqueous phase. Also, the extent of phase separation increases with the number of freeze–thaw cycles which leads to an increase in amylopectin retrogradation in the starch-rich phase (Yuan and Thompson, 1998). Hydrocolloids were found to be effective in retarding the retrogradation process of starch gels. A starch/ hydrocolloid interaction constitutes ways to improve the performance of starch gels (Sikora and Kowalski, 2007). Starch retrogradation changes with addition of hydrocolloids. In a study related to interaction of polysachharide gums and wheat starch dispersion during pasting, starch-hydrocolloid association was confirmed by differences in rates of starch retrogradation and changes in the physical properties of the resulting gels (Christianson et al. 1981).

Xanthan gum has been used extensively to stabilize the starch gels during freezing. Addition of xanthan gum (0.3% w/w) to corn starch pastes (10% w/w) has been found to minimize the amylose retrogradation, syneresis and rheological changes after freezing. However, its effect in preventing ice recrystallization and amylopectin retrogradation was not significant due to the fact that the gum acted outside the starch granule while amylopectin retrogradation took place within the granule (Ferrero et al., 1993, 1994, 1996). Sudhakar et al. (1996) reported that the water release after several freeze/ thaw cycles in corn starch and waxy *Amaranthus paniculatas* starch was reduced by addition of guar gum and locust bean gum. The reduction was high in guar gum added starches. This was attributed to a slowing rate of retrogradation brought about by the interaction between the hydrocolloid and amylose. Similarly, addition of xanthan gum, guar gum or sodium alginate to corn starch, sucrose or water mixtures minimized the structural damage to the gel/ paste after slow freezing and during frozen storage. The thermal studies revealed that the hydrocolloids did not change the *Tg*, but they might have interacted with the amylase released outside the granule, inhibiting the development of the spongy matrix (Ferrero and Zaritzky, 2000).

Lee et al. (2002) observed sodium alginate, guar gum and xanthan gum to be effective in reducing syneresis while curdlan, gellan gum and carrageenan were reported to increase syneresis of sweet potato starch gel after five freeze/ thaw cycles of sweet potato starch gel and storage at -18 °C for 20 h followed by 25 °C for 4 h. This may be due to alginate-water interaction and polymer interactions (Miwa *et al.*, 1993). Brennan et al. (2004) described that xanthan gum could reduce the retrogradation of waxy maize starch in rapid visco analyser and turbidimetric analysis. Xanthan gum also increased the freeze/ thaw stability after four cycles over a 4 weeks period. Effect of various hydrocolloids (xanthan gum, locust been gum, konjac-glucomannan and guar gum) on freeze-thaw cycles of tapioca gels was investigated by Muadklay and Charoenrein (2008). Reduction in syneresis was achieved with xanthan gum at 0.25 and 0.5 % concentrations than locust bean gum and konjac glucomannan. Guar gum was found to be ineffective in retarding the retrogradation. These authors concluded that the best conditions for reducing tapioca starch retrogradation were the addition of 0.50% xanthan gum and a fast freezing rate. Tran et al. (2008) suggested combination of modification in cassava starch (hydroxyl propylated or acetylated) and incorporation of xanthan or carboxy methyl cellulose to control freezable water in the starch gels. Xanthan gum was also found to reduce syneresis in tapioca starch gel after repeated freeze/ thaw cycles. Increase in pasting temperature, peak and final viscosities and a decrease in setback viscosity due to xanthan gum addition was reported and a positive correlation was found between setback and water separation (Pongsawatmanit and Srijunthongsiri, 2008).

Hydrocolloids have been reported to be effective in reducing syneresis of starch gels due to their good water holding capacity (Table 3). Different hydrocolloids have been found to stabilize the starch gels in different ways. The variation in their functionality for reducing syneresis depends on the chemical structure of the hydrocolloids added. William et al. (2009) reported Guar gum and xanthan gum to be very effective up to five freeze-thaw cycles in curdlan gel compared to k-carrageenan and locust beam gum. The highly substituted nature caused excellent hydration and hydrogen-bonding activity of these hydrocolloids which resulted in the zero syneresis (Hoyt 1966; Argin-Soysal *et al.* 2009). Xanthan gum was also observed to be the most effective in reducing syneresis of tapioca starch gels (Muadklay and Charoenrein (2008). Though syneresis was not seen in control tapioca gels (without xanthan gum) after three and five freeze-thaw cycles, it was because of change in tapioca gel texture to a spongy structure. Xanthan gum at 0.5 % concentration could retard change of texture in tapioca starch gel into a spongy structure after five repeated freeze–thaw cycles.

Some polysaccharides have also been reported to cause high syneresis and low stability of starch gel after freezing and thawing. Curdlan, gellan and k-Carrageenan gums increased syneresis to 81.4, 72.3, and 82.2%, respectively as compared to control gel which showed syneresis of 71.3 % (Lee et al., 2002). The adverse effects of these gums may be attributed to the three-dimensional polymer network that leads to formation of junction points of the polymer chains upon cooling leading to a more rigid structure of gel (Glicksman, 1982).

***Future perspectives***



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Advances in newer technologies of processing have broadened the range of food products with improved quality. Consumers are also becoming health and quality conscious. The demand for healthy, tasty and nutritious food products has created new opportunities for food components that improve appearance, texture and shelf-life. Hydrocolloids provide diversity and quality to processed foods. However, future thrust lies in the ability to select the proper hydrocolloid and to apply it in the proper way at optimum levels to meet the specific physical and organoleptic properties in the product. It is necessary to understand and establish relationships between the chemical structure, molecular structure and functional properties of hydrocolloids before any specific application. Furthermore, extent of modifications in the native forms of hydrocolloids should be done at acceptable levels to achieve the desired and controlled functional properties. Apart from chemical, physical and enzymatic modifications, fermentation could be used as a challenging technology to modify the hydrocolloids. Another challenge lies in the development and characterization of improved and cheap hydrocolloids from land and marine plants, microbial and animal sources. Apart from the functional attributes of the hydrocolloids, physiological benefits of them to humans needs to be researched.



## CONCLUSIONS

The applications of hydrocolloids as cryoprotectants offer new opportunities in freezing technology. Addition of hydrocolloids to bakery products reduces staling and also affects processing and product qualities. It stabilizes the texture of fish or meat muscle during processing and frozen storage. It retains the fresh like texture in frozen fruits and vegetables. Hydrocolloids in ice-cream have been proved to improvise the texture, taste; melting characteristics as well to reduce sandiness and re-crystallization. Hydrocolloids not only protect the food products from deleterious affects of freezing and frozen storage but also help to design and develop novel frozen products with extended shelf-life. However, functionality of hydrocolloids greatly depends on its physico-chemical characteristics as well as the constituents of the system to which it is added. Effect of individual hydrocolloid and/ or interaction of various hydrocolloids may differ in the final product quality or freezing stability. Hence, a balance between improved frozen-stability and good processing efficiency is required to deliver a good quality frozen food product.

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**Table 1** List of various hydrocolloids used in food applications

| Hydrocolloid | Source | Structural unit | Property | Functionality | Reference |
|---|---|---|---|---|---|
| Agar | Red seaweeds (*Rhodophycae*); Species of *Gelidium* and *Gracilariae* | Agar consists of a mixture of agarose and agaropectin | Agar is insoluble in cold water | Agar has a major use in microbiological media. It is used in icings, glazes, processed cheese, jelly sweets and marshmallows. | Miwa et al., 1993 |
| Alginate | Produced by brown seaweeds (*Phaeophyceae*; Species *Laminaria*) | Alginates are linear unbranched polymers containing β-(1→4)-linked D-mannuronic acid (M) and α- | Solubility and water-holding capacity depend on pH, molecular weight, | Alginates are thermally stable cold setting gelling agents. They show high water | Miwa et al., 1993 |

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| | | (1→4)-linked L-guluronic acid (G) residues | ionic strength and the nature of the ions present | absorption and used as low viscosity emulsifiers and shear-thinning thickeners. They can be used to stabilize phase separation in low fat fat-substitutes | |
| Carrageenan | Red seaweed (*Rhodophycae*); genus *Chondrus*, *Eucheuma*, *Gigartina* and *Iridaea*. | Carrageenan consists of alternating 3-linked-β-D-galactopyranose and 4-linked-α-D-galactopyranose | κ- and ι-carrageenans form thermo-reversible gels on cooling in the presence | Carrageenans are used mainly for thickening, suspending and gelling. Used as a binder in | Nussinovitch, 1997 |

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| | | units | of appropriate counter ions | cooked meats, to firm sausages and as a thickener in toothpaste and puddings. | |
| Carboxymethyl cellulose | Derivative of cellulose formed by its reaction with alkali and chloroacetic acid. | CMC structure is based on the β-(1→4)-D-glucopyranose polymer of cellulose | Dissolve rapidly in cold water | Used for controlling viscosity without gelling | Miwa et al., 1993 |
| Cellulose | Found in plants as microfibrils; mostly prepared from wood pulp | Cellulose is a linear polymer of β-(1→4)-D-glucopyranose units | Insoluble in water. Bacterial cellulose (*ex.* | Used as an anticake agent, emulsifier, stabilizer, | Nussinovitch, 1997 |

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| | | | *Acetobacter xylinum*), with much smaller fibrils than plants fibrils, exhibits pseudoplastic viscosity | dispersing agent, thickener, and gelling agent | |
| Curdlan | It is a microbial fermentation extracellular polymer; prepared from a mutant strain of *Alcaligenes faecalis* var. *myxogenes*. | A moderate molecular weight unbranched linear 1→3 β-D glucan with no side-chains. | Insoluble in cold water; Salts tend to prevent curdlan from gelling | Curdlan gum is tasteless and produces retortable freezable food elastic gels | Miwa et al., 1993 |
| Gelatin | Collagen from animal by-products | Mixture of proteins and polypeptides | Soluble in water | Gelatin is multi-functional. It | Karim & Bhat, 2008 |

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| | | | | is used as a gelling, thickening, water-binding, emulsifying, foaming, film-forming agent | |
| Gellan Gum | It is a bacterial exopolysaccharide; prepared by aerobic submerged fermentation from *Sphingomonas elodea* | A linear tetrasaccharide →4)-L-rhamnopyranosyl-(α-1→3)-D-glucopyranosyl-(β-1→4)-D-glucuronopyranosyl-(β-1→4)-D-glucopyranosyl-(β-1→ with O(2) L-glyceryl and O(6) acetyl | In acylated form gellan forms soft, elastic, transparent and flexible gels but once de-acylated it forms hard, non-elastic brittle gels | Gellan gum is used as a gelling, texturizing and suspension hydrocolloid and is functional at very low levels in the presence of ions | Donner and Douds, 1995 |

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| | | substituents on the 3-linked glucose | | | |
| Guar gum | It is extracted from the seed of the leguminous shrub *Cyamopsis tetragonoloba* | It is a galactomannan consisting of a (1→4)-linked β-D-mannopyranose backbone with branches from their 6-positions linked to α-D-galactose | Hydrates fairly rapidly in cold water; does not form gels; shows high low-shear viscosity | Guar gum is an economical thickener and stabilizer | Miyazawa, 2006; Rodge et al., 2012 |
| Gum arabic | It is prepared from exudate from the stems and branches of *Acacia senegal* and *Acacia seyal* trees | It is a complex and variable mixture of arabinogalactan oligosaccharides, polysaccharides and glycoproteins | It is readily soluble to give relatively low viscosity newtonian solutions | It is a useful hydrocolloid emulsifier, texturizer and film-former; widely used in the drinks | Nussinovitch, 1997 |

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| | | | even at high concentrations. | industry to stabilize flavors and essential oils; also used in confectionery | |
| Gum tragacanth | It is an exudate gum from *Astragalus gummifer* | It consists of a mixture of polysaccharides including an arabinogalactan containing α-L-arabinofuranose and 1-4-linked β-D-galalactopyranose and an acidic complex poly-1-4-linked α-D-galalacturonate | | It is used as an acid-resistant thickener and emulsifier in sauces, salad dressings and confectionery lozenges. | Miwa et al., 1993 |
| Locust Been | It is extracted | It is a | It needs | Retards ice | Barak and |

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| Gum | from the seed (kernels) of the carob tree (*Ceratonia siliqua* | galactomannan consisting of a (1→4)-linked β-D-mannopyranose backbone with branches from their 6-positions linked to α-D-galactose | heating to dissolve but is soluble in hot water | crystal growth by forming structured gel at solid/liquid interface | Mudgil (2014) |
| Pectin | It makes up between about 2% and 35% of plant cell walls. It is found in fruit and vegetables; prepared from 'waste' citrus peel and apple pomace. | Pectin has a complex structure with an α-(1→4)-linked D-galacturonic acid polysaccharide backbone | Low methoxyl pectins (< 50 % esterified) form thermo-reversible gels in the presence of calcium ions and at low | Pectins are mainly used as gelling agents, but can also act as thickener, water binder and stabilizer | May, 1990; Thakur et al., 1997 |




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| | | | pH whereas high methoxyl pectins forms thermally irreversible gels in the presence of sufficient sugars at low pH | | |
| Starch | It is the major carbohydrate reserve in plant tubers and seed endosperm. The largest source of starch is corn (maize) with other commonly used sources | Starch consists of two types of molecules, amylose (normally 20-30%) and amylopectin (normally 70-80%). Both consist of | As they absorb water, they swell, lose crystallinity and leach amylose. The higher the amylose content, the | Used as thickener, water binder, emulsion stabilizer and gelling agent. | Singh et al., 2003 |

| | | | | | |
|---|---|---|---|---|---|
| | being wheat, potato, tapioca and rice. | polymers of α-D-glucose units. | lower is the swelling power and the smaller is the gel strength for the same starch concentration. | | |
| Xanthan Gum | It is a microbial desiccation-resistant polymer; prepared by aerobic submerged fermentation from *Xanthomonas campestris*. | Xanthan gum has a β-(1→4)-D-glucopyranose glucan backbone with side chains of (3→1)-α-linked D-mannopyranose-(2→1)-β-D-glucuronic acid-(4→1)-β-D-mannopyranose | It hydrates rapidly in cold water without lumping; it has high low-shear viscosity and shear-thinning character. | Used as thickener, stabilizer, emulsifier and foaming agent. | Garcia-Ochoa et al., 2000 |

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| | | on alternating residues. | | | |



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**Table 2** Effect of different hydrocolloids on loaf volume of bread made from frozen dough

| Hydrocolloid | Frozen storage (days) | Loaf specific volume ($cm^3$/100 g) | | Reference |
|---|---|---|---|---|
| | | Without hydrocolloid | With hydrocolloid | |
| Guar gum (0.5 %) | 60 | 330 | 385 | Ribotta et al (2004) |
| k-Carrageenan (0.5%) | 42 | 386 | 366 | Barcenas et al. (2004) |
| HPMC (0.5 %) | 42 | 386 | 406 | Barcenas et al. (2004) |
| Xanthan gum (0.1 %) | 30 | 242 | 254 | Dodic et al. (2007) |
| k-Carrageenan (1 %) | 30 | 242 | 251 | Dodic et al. (2007) |
| CMC (1 %) | 30 | 242 | 251 | Dodic et al. (2007) |
| Gum Arabic (3 %) | 112 | 364 | 593 | Sharadanant and Khan (2003) |
| CMC (3 %) | 112 | 375 | 497 | Sharadanant and Khan (2003) |
| k-Carrageenan (3 %) | 112 | 374 | 512 | Sharadanant and Khan (2003) |
| Locust bean Gum (3%) | 112 | 367 | 624 | Sharadanant and Khan (2003) |

**Table 3** Effect of various hydrocolloids in controlling syneresis of frozen gels after freeze-thaw cycles

| Gel Type | Hydrocolloid | Concentration of hydrocolloid (%) | Syneresis as a function of number of freeze-thaw cycles | | |
|---|---|---|---|---|---|
| | | | 1 | 3 | 5 |
| Rice starch gel[1] (8 %) | Konjac glucomannan | 0.00 | 62.5 | 66.0 | 69.9 |
| | | 0.30 | 32.0 | 56.6 | 64.9 |
| | | 0.50 | 21.5 | 43.5 | 49.7 |
| Curdlan gel[2] (1 %) | κ Carrageenan | 1.00 | 18.6 | 17.7 | 15.6 |
| | Guar Gum | 1.00 | ND | ND | ND |
| | Locust Bean Gum | 1.00 | 31.6 | 46.8 | 59.6 |
| | Xanthan gum | 1.00 | ND | ND | ND |
| Tapioca starch gel[3] (5 %) | Xanthan gum | 0.00 | 35.2 | ND | ND |
| | | 0.25 | 5.7 | 60.8 | ND |
| | | 0.50 | 0.6 | 60.5 | 67.7 |
| Sweet potato starch gel[4] (7%) | Without any gum | 0.00 | - | 71.3 | - |
| | Alginate | 0.60 | - | 41.2 | - |
| | κ Carrageenan | 0.60 | - | 82.2 | - |
| | CMC | 0.60 | - | 66.4 | - |

| | | | | | |
|---|---|---|---|---|---|
| | Curdlan | 0.60 | - | 81.4 | - |
| | Gellan | 0.60 | - | 72.3 | - |
| | Guar | 0.60 | - | 21.8 | - |
| | Gum Arabic | 0.60 | - | 62.8 | - |
| | Locust bean | 0.60 | - | 56.8 | - |
| | Xanthan gum | 0.60 | - | 46.8 | - |

[1]Charoenrein et al. (2011)

[2]William et al. (2009)

[3]Muadklay and Charoenrein (2008)

[4]Lee et al. (2002)

ND: mean not detected