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EMULSIFYING PROPERTIES OF OXIDIZED AFRICAN STAR APPLE (*CHRYSOPHYLLUM AFRICANUM*) GUM

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ABSTRACT: *African star apple gum was oxidized using hydrogen peroxide at 60 ºC for 4 hours. The oil binding capacity, hydrodynamic volume, insoluble gel and flow property of the native and oxidized gums were compared. The XRD analysis of the native and oxidized gums was carried out. The oil binding capacity and hydrodynamic volume of the native gum were 6.83 g and 3117 d.nm respectively. On oxidation, the oil binding capacity and flow properties of the gum increased while the hydrodynamic volume and the insoluble gel reduced. The insoluble gel reduced from 58.61 to 48.32 %. XRD revealed a decrease in crystallinity as the degree of oxidation increased. The emulsification capacity of African star apple gum reduced as oxidation increased.*

KEYWORDS: African star apple, *Chrysophyllum africanum*, gums, oxidation, emulsification

INTRODUCTION

With over 2500 permitted additives, emulsifiers are very essential additives in the food and pharmaceutical industry (Carocho *et al*., 2014). According to the European Union emulsifiers are one of the twenty-six (26) groups of additives along with sweeteners, colourants and flavor enhancers (Huvaere *et al*., 2012; Stevens *et al*., 2014). An emulsion consists of a mixture of two immiscible liquids where droplets of one are incorporated within the other (Kralova and Sjöblom, 2009). Emulsions are essential parts of food systems and pharmaceutical formulations. In emulsions, there is a continuous phase and the dispersed phase interreacting with each other. Emulsions can be divided into coalesce, flocculate or separate. The difference in specific gravity often causes the continuous phase to separate as droplets begins to aggregate. This results in loss of creamy feel in ice-cream when frozen for long periods (McClments, 2015).

Emulsifiers are able to enhance appearance and improve organoleptic properties. They are also used to provide other nutritional benefits or encapsulate unpleasant aroma. (Halmos *et al*., 2018). Emulsifiers due to their amphiphilic nature are able to adsorb to droplets of oil and water as soon as they are formed. They have both hydrophilic and hydrophobic parts which is effective in adsorption at the interface of oil-water systems (Hasenhuettl, 2008).

While the use of synthetic non-ionic polysorbates began in 1930s as part of margarine formulations and in baking to prevent stalling and enhance firmness and volume (Hasenhuettl, 2008), studies (Cani and Everard, 2015; Arnold and Chassaing, 2019) have reported that synthetic emulsifiers are potentially harmful to the digestive tract causing inflammatory bowel disease and early life intestinal stress. Natural emulsifiers on the other hand even at high concentrations are more beneficial (Blesso *et al*., 2013)

Gums are able to function as both emulsifiers and weighting agents. Gums Arabic and xanthan gum have been used as stabilizer and emulsifier (Zecher and Van Coillie, 1992). This study compares the changes in physicochemical properties of African star apple gum after oxidation and the changes in its emulsifying capacity.

METHODOLOGY

Sample Collection and gum extraction

Ripe African star apple fruits were obtained from local market in Kaduna state, Nigeria and authenticated. After washing and removing foreign contaminants, the fruits were peeled and the pulp was soaked in water for three days. The solution was filtered and ethanol was added to obtain the african star apple gum. The gum was washed with acetone to remove impurities and was then kept in a desiccator for further analysis (Ayorinde *et al*., 2018).

Oxidation of gum

10 % African Star apple gum was prepared in a 250 ml beaker and 10 ml of hydrogen peroxide was added. The beaker and its content were stirred in a preheated water bath at 60 ºC for 4 hours at 20 minutes interval. Pure oxidized gum was extracted with ethanol and washed with acetone. The procedure was repeated with 20, 30, 40 and 50 ml of hydrogen peroxide. The samples were labelled OX 60 1, OX 60 2, OX 60 3, OX 60 4, OX 60 5 respectively (Lu *et al*., 2019).

Determination of Carboxyl Percentage

The carboxyl content was determined by the method of Lu *et al*. (2019). 0.045 g each of the gums were dissolved in 30 ml water with continuous stirring. 10 ml of 0.1 M calcium acetate was added and the mixture was stirred for 1 hour before it was titrated with 0.01 M NaOH. The carboxyl content was calculated using Equation 1.

$$\text{Carboxyl \%} = \frac{(\text{Vol of oxidized gum} - \text{Vol of native gum}) \times 0.01 \times 45}{0.045} \times 100\% \qquad (1)$$

Water Binding and Oil binding Capacity

0.25 g of each gum sample was weighed in pre-weighed graduated centrifuge tube and 10 ml of water was added to each. After 20minutes the new weight was recorded before centrifuging the mixture at 3000 rpm for 20 minutes. The supernatant was discarded and the tube re-weighed with its content. Sample and centrifuge tube weight were deducted from the new weight and difference in weight was recorded as the water absorption capacity of the gum. The oil binding capacity was carried out with the same procedure while was used instead of water (Afolabi and Adekanmi, 2017).

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Compressibility Index

50 ml measuring cylinder was filled up to the 10 ml mark with the gum sample. The bulk density (g/cm^3) of the dry gum was determined by dividing the weight of the gum in the measuring cylinder by its volume (10 ml). The tap density (g/cm^3) was determined by subjecting the gum powder in the measuring cylinder (above) to 100 taps. For the tapped density, the weight of the gum is divided by the new volume (Nep and Conway, 2011; Afolabi, 2012). The compressibility index (Carr's index) was determined using equation 2.

$$\text{Carr's Index} = \frac{\text{Bulk density} - \text{Tapped dnsity}}{\text{Bulk density}} \times 100\% \qquad (2)$$

Dynamic Light Scattering (DLS)

The hydrodynamic volume and size distribution of the gum samples were determined in a Malvern Zetasizer 7.01 using water as dispersant. The hydrodynamic diameter. d(h) of sample in solution is calculated from the translational diffusion coefficient applying the Stokes−Einstein equation:

$$d(h) = \frac{kT}{3\pi\eta D} \qquad (3)$$

Here, T is the absolute temperature, k is the Boltzmann's constant, D is the translational diffusion coefficient, and η is the viscosity of the solvent.

XRD analysis of the gums

0.2 g of the dry gum powder was placed on clean flat sample holder to form a smooth and flat pellet. The pellet was mounted on the sample stage in the XRD cabinet. X-ray diffractograms were recorded by a copper anode X-ray tube using an Analytical Diffractometer (Pan Analytical, Phillips, Holland). The diffractometer was operated at 40 mA and 45 kV with a scanning speed of 4°/min. The diffractometer was operated continuously between 2θ angles of 5° and 79° (Singh *et al*., 2012).

Emulsion capacity and emulsion stability test

The method of Onweluzo *et al*. (1995) was used with modification. 0.25 g of each gum sample was blended with 10 ml of distilled water at room temperature for 30 seconds. After complete dispersion 10 ml of groundnut oil was added and blended for 5 minutes. The mixture was poured into a graduated 30 ml bottle and shaken vigorously. The volume of the emulsified layer was read directly from the tube. The stability of the emulsion layer was monitored over four weeks by recording the emulsion capacity in the first seven days and at the end of the second, third and fourth weeks. Emulsification Capacity is calculated as shown below:

$$\text{Emulsification Capacity (\%)} = \frac{\text{Height of emulsified layer}}{\text{Height of the whole solution in the centrifuge tube}} \times 100\ \%$$

DISCUSSION

Insoluble gel and Oil binding capacity

African Star apple gum is over 54 % insoluble. The insoluble part of the native gum also now as the insoluble gel gives the material potential for biosorption. The insoluble gel also has pharmaceutical application as a viscosity enhancer and in controlled drug release. Oxidation reduced the insoluble gel of the gums through depolymerization. The increase in hydrophilic functional group (-COOH) also reduced the insoluble gel of the gum. At elevated temperature, the insoluble gel reduces even further. The oil binding capacity of the native gum was 6.83 g. Due to the increase in intermolecular space, the oil binding capacity of the oxidized gums increased.

Hydrodynamic volume and Flow properties

The hydrodynamic volume of the oxidized gums reduced as the degree of oxidation increased. Since depolymerization results in reduction in chain length of the gum polymeric molecules and there is a consequent reduction in the number of carboxyl group per chain. As a result, the amount of water molecules that can be attached to each chain reduces (Wu *et al*., 2017). Similarly, the tapped and bulk densities of the oxidized gums reduced. Carr's index quantifies the flowability of a material (Ohwoavworhua and Adelakun 2005). Gums with good flowability have Carr's index value lower than 26 (Afolabi and Adekanmi, 2017). The Carr's index of the gums all fall within this range; hence good flowability.

XRD Analysis

The diffractogram of the native gum revealed crystalline regions although largely amorphous. The semicrystaline nature is attributed to intermolecular hydrogen bonding (Pandit *et al*., 2019; Afinjuomo *et al*., 2020). Oxidation reduced the number and intensity of the peaks observed. This implies a reduction in crystallinity through a ring opening process making the gum more amorphous (Ali *et al*., 2018; Ziegler-Borowska, 2018; Afinjuomo *et al*., 2020).

Emulsification Stability

Emulsification capacity decreased with increase in degree of oxidation of the gum. The differences recorded were attributed to the protein content, level of solubility and particle size of the gums. These factors determine their interaction with the oil water system (Riquelme *et al*., 2020). Although the solubility and water absorption capacity of the oxidized gum increased, their emulsification capacity reduced. Depolymerization through oxidation causes reduction in chain length, molecular weight, hydrodynamic volume and particle size as the degree of oxidation increase. Higher turbidity in oil water system is typical of good emulsifiers. Gums with high molecular weight and high protein content are also better emulsifiers (Dickinson *et al*., 1991; Yadav *et al*., 2007).

Sample	NATIVE	OX 60 1	OX 60 2	OX 60 3	OX 60 4	OX 60 5
Carboxyl content (%)		36.03 ± 0.02	42.35 ± 0.02	49.04 ± 0.04	54.06 ± 0.02	57.06 ± 0.01
Oil Binding Capacity (g)	6.83 ± 0.03	6.88 ± 0.02	6.91 ± 0.01	6.95 ± 0.01	6.99 ± 0.03	7.05 ± 0.00
Cold water insoluble gel (%)	54.61 ± 0.07	52.04 ± 0.05	51.25 ± 0.07	50.40 ± 0.05	49.77 ± 0.01	48.32 ± 0.02
Hot water insoluble gel (%)	36.70 ± 0.02	34.46 ± 0.03	30.60 ± 0.04	28.87 ± 0.01	25.16 ± 0.01	23.22 ± 0.02
Hydrodynamic diameter (d.nm)	3117	3067	2954	2681	2396	2016
Bulk density (g/cm3)	0.567 ± 0.001	0.566 ± 0.000	0.564 ± 0.001	0.561 ± 0.000	0.557 ± 0.002	0.552 ± 0.000
Tapped density (g/cm3)	0.627 ± 0.002	0.626 ± 0.001	0.625 ± 0.000	0.623 ± 0.002	0.621 ± 0.002	0.617 ± 0.001
Carr's Index	10.610 ± 0.122	10.600 ± 0.083	10.816 ± 0.12	11.052 ± 0.114	11.490 ± 0.122	11.775 ± 0.095

Table 1: Properties of oxidized African star apple gums

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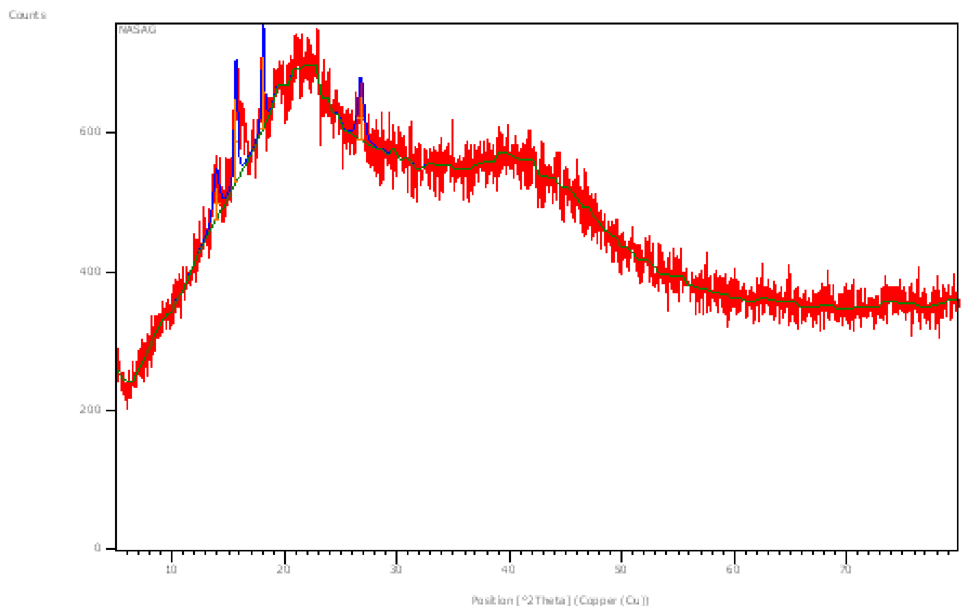

Figure 1: XRD result for Native African Star Apple gum.

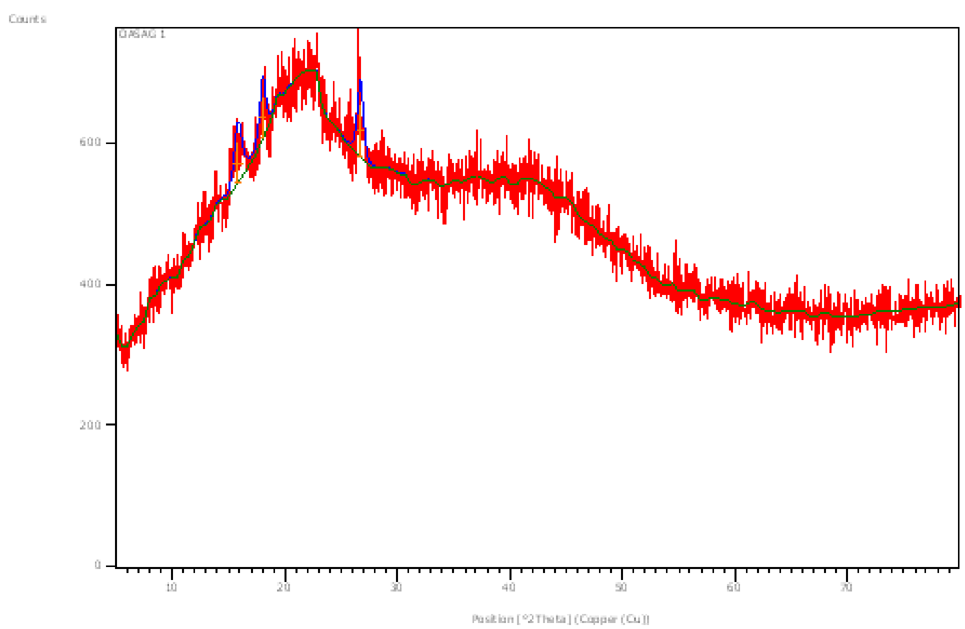

Figure 2: XRD result for oxidized African Star apple gum (OX 60 1).

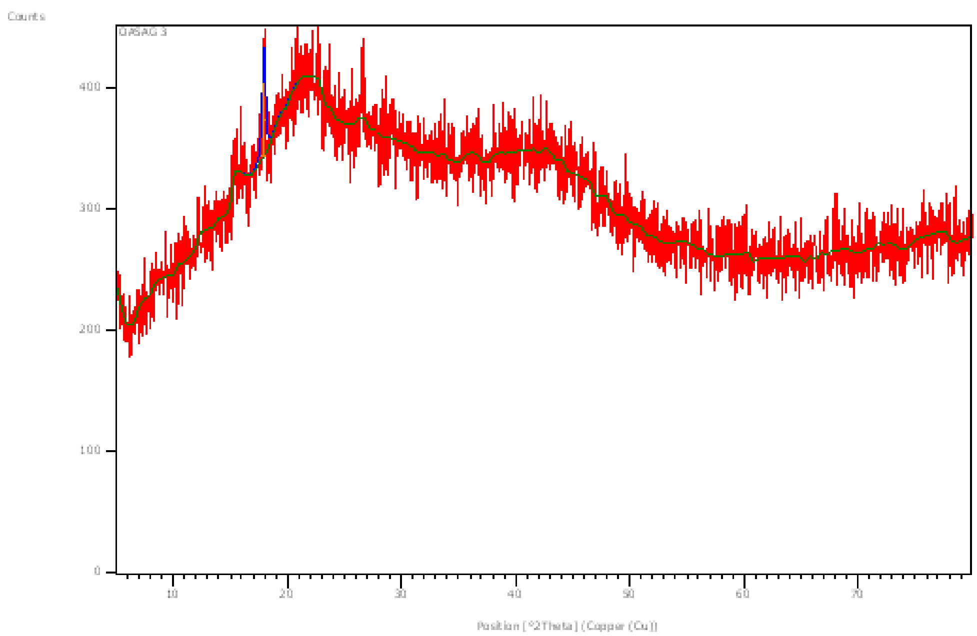

Figure 1: XRD result for oxidized African Star apple gum (OX 60 3).

Table 4: Emulsification Capacity Stability (%) of native and oxidized African Star Apple gum in Week 1

Sample	Day 1	Day 2	Day3	Day 4	Day 5	Day 6	Day 7
NATIVE	50.28 ± 0.01	45.79 ± 0.02	41.62 ± 0.05	34.25 ± 0.10	28.15 ± 0.08	25.76 ± 0.05	21.34 ± 0.08
OX 60 1	50.28 ± 0.02	45.05 ± 0.08	41.00 ± 0.08	34.15 ± 0.11	27.48 ± 0.10	24.84 ± 0.12	20.42 ± 0.15
OX 60 2	50.50 ± 0.05	45.05 ± 0.09	41.00 ± 0.10	34.15 ± 0.12	27.48 ± 0.15	24.84 ± 0.15	20.42 ± 0.13
OX 60 3	50.50 ± 0.08	32.85 ± 0.11	41.00 ± 0.09	34.15 ± 0.10	27.48 ± 0.13	24.84 ± 0.11	20.42 ± 0.12
OX 60 4	40.00 ± 0.02	32.85 ± 0.03	29.75 ± 0.08	25.01 ± 0.10	21.56 ± 0.08	18.28 ± 0.11	15.95 ± 0.14
OX 60 5	40.00 ± 0.08	32.85 ± 0.09	29.75 ± 0.10	25.01 ± 0.07	21.56 ± 0.11	18.28 ± 0.13	15.95 ± 0.11

Table 4: Emulsification Capacity Stability (%) of native and oxidized African Star Apple gum in week 2, week 3 and week 4

Sample	Week 2	Week 3	Week 4
NATIVE	20.15 ± 0.10	19.55 ± 0.09	19.55 ± 0.08
OX 60 1	19.40 ± 0.10	19.40 ± 0.03	19.40 ± 0.05
OX 60 2	19.40 ± 0.09	19.40 ± 0.04	19.40 ± 0.02
OX 60 3	19.40 ± 0.11	19.40 ± 0.06	19.40 ± 0.04
OX 60 4	15.02 ± 0.10	15.02 ± 0.05	15.02 ± 0.09
OX 60 5	15.02 ± 0.05	15.02 ± 0.04	15.02 ± 0.04

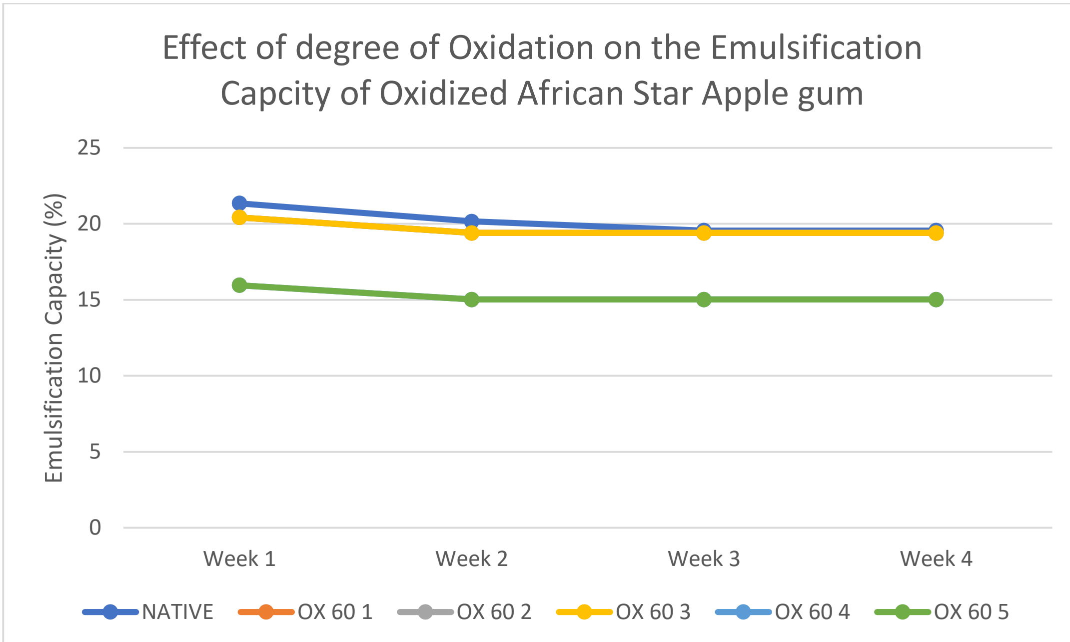

Figure 4: Effect of degree of Oxidation on the Emulsification Capacity of Oxidized African Star Apple gum.

CONCLUSION

Oxidation of African star apple gum increased it water and oil absorption capacity. The oxidized gums have good flow properties as indicated by the carr's index. Loss of crystallinity and reduced particles size also compliment the material as a binder in pharmaceuticals. Although the solubility of the gum increased, the insoluble gel and emulsification properties of the oxidized gums reduced as the degree of oxidation increased. This makes the gum a viable mild emulsifier for cosmetics, pharmaceutical and confectionary application.

REFERENCES

Afinjuomo, F., Paris, F., Barclay, T. G., Song, Y., Petrovsky, N. and Garg, S. (2020) Influence of Oxidation Degree on the Physicochemical Properties of Oxidized Inulin. *Polymers* 12: 1205-1025.

Afolabi, A. (2012). Synthesis and physicochemical properties of carboxymethylated bambara groundnut (*Voandzeia subterranean*) starch. *International journal of food science and technology* 47: 445- 451.

Afolabi, T. A. and Adekanmi, D. G. (2017) Characterization of Native and Graft Copolymerized *Albizia* gums and Their Application as a Flocculant. *Journal of Polymers* 2017: 1-8. doi:10.1155/2017/3125385.

Ali, A., Ganie, S. A. and Mazumdar, N. (2018) A new study of iodine complexes of oxidized gum arabic: An interaction between iodine monochloride and aldehyde groups. *Carbohydrate*

Polymers 180: 337–347.

Arnold, A. R. and Chassaing, B. (2019) Maltodextrin, Modern Stressor of the Intestinal Environment. *Cellular and Molecular Gastroenterology and Hepatology* 7: 47 5–476.

Ayorinde, J. O., Effiong, D. E. and Odeniyi, M. A. (2018) Design and Evaluation of Oral Dissolving Films of Chlorpheramine From Native and Modified Enterolobium cyclocarpum Gum. *African Journal of Biomedical Research* 21: 175- 182.

Blesso, C. N., Andersen, C. J. and Barona, J. (2013) Whole egg consumption improves lipoprotein profiles and insulin sensitivity to a greater extent than yolk-free egg substitute in individuals with metabolic syndrome. *Metabolism* 62: 400–410.

Cani, A. and Everard, P. D. (2015). Keeping gut lining at bay: impact of emulsifiers. *Trends in Endocrinology and Metabolism* 26: 273 – 274.

Carocho, M., Barreiro, M. F. and Morales, P. (2014) Adding molecules to food, pros and cons: A review on synthetic and natural food additives. *Comprehensive Reviews in Food Science and Food Safety* 13: 377– 399.

Dickinson, E. (1991) The role of hydrocolloids in stability particulate dispersions and stabilizer for the industry for the food Industry (Vol. 4). (P. W. A., Ed.) Oxford: IRL Press.

Halmos, E. P., Mack, A. and Gibson, P. R. (2019) Review article: Emulsifers in the food supply and implications for gastrointestinal disease. *Alimentary Pharmacology and Therapeutics* 49: 41– 50.

Hasenhuettl, G. L. (2008) *Food Emulsifiers and Their Applications.* New York: Springer Science Business Media.

Huvaere, K., Vandevijvere, S. and Hasni, M. (2012) Dietary intake of artificial sweeteners by the Belgian population. *Food Additives and Contaminants: Part A* 29: *54– 65.*

Kralova, I. and Sjöblom, J. (2009) Surfactants used in food industry: a review. *Journal of Dispersion Science Technology*. 30: 1363- 1383.

Lu, Y., Zhao, X. and Fang, S. (2019) Characterization, Antimicrobial Properties and Coatings Application of Gellan Gum Oxidized with Hydrogen Peroxide. *Foods* 8: 31-43.

McClements D. J. (2015) *Food Emulsions Principles, Practices, and Techniques.* Boca Raton, FL: CRC Press; Group, Taylor and Francis.

Nep, E. I. and Conway, B. R. (2011) Physicochemical characterization of grewia polysaccharide Gum: Effect of drying method. *Carbohydrate Polymer* 84: 446–453.

Ohwoavworhua, F. O. and Adelakun, T. (2005) Some physical characteristics of microcrystalline cellulose obtained from raw cotton of Conchlospermum planchonii. *Tropical Journal for Pharmaceutical Research* 4 (2): 501-507.

Onweluzo, J. C., Onuoha, K. C. and Obanu, Z. A. (1995) Certain functional properties of gums derived from some lesser-known tropical legumes (*Afdzelia africana, Dtarium microcapum* and *Mucuna flagellipes*). *Plant Food Human Nutrition* 48: 55–63.

Pandit A. H., Mazumdar N., Imtiyaz K., Rizvi M. M. A. and Ahmad S. (2019) Periodate-Modified Gum Arabic Cross-linked PVA Hydrogels: A Promising Approach toward Photoprotection and Sustained Delivery of Folic Acid, *American Chemical Society*, 2019 (4): 16026-16036 DOI: 10.1021/acsomega.9b02137

Partridge, D., Lloyd, K. A., Rhodes, J. M. and Walker, A. W. (2019) Food additives: Assessing the impact of exposure to permitted emulsifiers on bowel and metabolic health – introducing the FADiets study. *Nutrition Bulletin* 44: 4.

Riquelme, N., Robert, P., Troncoso, E. and Arancibia, C. (2020). Influence of the particle size and hydrocolloid type on lipid digestion of thickened emulsions. *Food and Function, 11*, 5955-5964.

Stevens, L. J., Burgess, J. R. and Stochelski, M. A. (2014) Amounts of artificial food colors in commonly consumed beverages and potential behavioural implications for consumption in children. *Clinical Pediatrics* 53: 133– 140.

Singh H., Sodhi N. S. and Singh N. (2012) Structure and Functional Properties of Acetylated Sorghum Starch, *International Journal of Food Properties*, 15 (2), 312-325, DOI: 10.1080/10942912.2010.483633

Wu, Y., Cui, W., Eskin, N. A. and Goff, H. D. (2009). Fractionation and partial characterization of non-pectic polysaccharides from yellow mustard mucilage. *Food Hydrocolloids* 23: 1535-1541.

Yadav, M. P., Fishman, M. L., Chau, H. K., Johnston, D. B. and Hicks, K. B. (2007) Molecular characteristics of corn fiber gum and their influence on its emulsifying properties. *Cereal Chemistry.* 84 (2): 175-180.

Zecher, D. and Van Coillie, R. (1992) Cellulose derivatives: Thickening and gelling agents for food. London: Blackie Academic and Professional.

Ziegler-Borowska, M., Wegrzynowska-Drzymalska, K., Chelminiak-Dudkiewicz, D. Kowalonek, J. and Kaczmarek, H. (2018) Photochemical Reactions in Dialdehyde Starch. *Molecules* 23: 3358.