Use of Renewable Milk Raw Materials in the Printing and Related Industries

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Abstract: Nowdays, there is a growing desire to increase the use of renewable materials in the production process materials and by reducing pollution during the production process in which they are used. Synthetic and non-renewable raw materials do not affect the environment only in the phase of production of products but also in printing proces and after of use of products. In the graphic industry mentioned materials affect to printability, recyclability, and biodegradability. Synthetic polymers fill the paper pores and/or form a layer at the surface of the paper, causing a loss of part of the raw material in recovery or recycling process. Biopolymers as naturally renewable resources are increasingly used in graphic materials. One of the important raw materials are milk proteins casein and whey, which, in addition to sustainability, also give good qualitative properties graphical materials. The mentioned raw material has its use in paper coatings, inks, and adhesives.

Keywords: Milk, renewable raw material, printing industry.

INTRODUCTION

In all fields of industry, including the graphic and its accompanying industries, there is a growing desire to increase the sustainability of the production process and products. To understand the impact of these industries on the environment, much research has been done. Pulp, paper, and printing industries have dropped GHG emissions in Europe from 3% to 0.6% from 1990 to 2008, while production has increased by around 12%. The European Commission EC defined its 20/20/20 mandatory reduction targets by 2020 (20% reduction of GHGs / 20% increase in energy efficiency / 20% increase of renewable energy sources). The pulp and paper industry are one of the world's largest users of renewable, low-carbon energy. Around 50% of the primary energy used to make paper in Europe and the US comes from carbon neutral renewable resources and over 50% of its raw materials for production coming from recovered products [1, 2].

Carbon dioxide and other greenhouse gases are the indicators for emissions of consumption of non-renewable energy in the production of materials and transport as well use of non-renewable raw materials in the production. Volatile organic compounds (VOC) and organic hazardous air pollutants (HAP) indicate emissions in the printing process as dyeing processes, ink mixing operations, laminating and postpress processes. ROC and SR compounds indicate the pollution emitted in the papermaking processes. Some of the VOC compounds emitted during the printing process are pentanol, o-xylene, n-hexane, xylene and others [3,4]. The amount of compounds emitted depends on the printing technique and technology used. Said compounds affect stratospheric ozone depletion and ground level ozone formation which may affect LA-type smog formation. The greenhouse effect is another effect to which VOCs directly contribute. Accumulating the mentioned compounds in the area in the troposphere and absorbing infrared radiation from the sun or the earth The emission of VOCs is especially significant in printing hause because it affects the toxic and carcinogenic health of people, must be mentined that the vapors can be safety hazardous. The retention time of VOCs of compounds in the external atmosphere is depending on the removal mechanism from the troposphere which may be dry and wet deposition or by chemical reactions. From indoor atmosphere thay can be purifyed in different ways. Water-based inks do not produce VOCs emissions.

In the study Hansuebsai at al were measured VOC emissions emited by using of printing materials such as inks, coatings and glues, which were calculated according to the PNEAC method. VOC content values in inks are 35% / kg, in overprint varnish 75% / kg and in binging glue 35% / kg [5]. It can be seen from the above that the graphic industry has a significant impact on the environment.

To reduce the impact on the environment and people fossil fuel-based raw materials are being replaced with renewable and environmentally friendly raw materials, and alternatives and new formulations of product are being developed. Biobased polymers have a high potential in this area. Such compounds possess properties such as sustainability, biodegradability, non-toxicity, and biocompatibility [6, 7].

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Some of the biopolymers have been used since ancient times when they were made by hand until today when they are made in industrial plants. Their formulation has been perfected in recent years to obtain various desirable properties. Examples of such products are casein-based adhesives, which in new formulations have improve properties such as resistance to weathering and water, fast reversible adhesion, long life, and mold resistance, etc. [8]. Some biopolymers have been used since the middle of the last century when technological processes and tests have enabled the possibility of their industrial production with already some advanced properties that are still being refined, as whey protein-based adhesives. In this study, special attention will be given to milk proteins, casein, and whey proteins. The difference between the mentioned proteins is in the chemical state and structure, different amino acid compositions, protein conformation and phosphorylation of the casein protein.

Caseins have a major fraction of milk proteins, the pH value of their isoelectric point is 4.6 where the precipitating process occurs. Casein in milk can be mostly found in a colloidal form of micelles in about 85-90% [6]. The molecular geometry has a shape spherical aggregates with interactions via hydrophobic and electrostatic interactions and calcium bridging. The described interactions methods allow connection about 10,000 casein molecules [7]. Casein consists of proteins αS1-casein (36%), αS2-casein (10%), βcasein (36%), and κ-casein (13%), which are stabilized by the creation of a micellar structure due to their highly hydrophobic nature [9]. Just like casein and whey proteins, casein proteins differ from each other in their amino acid, phosphorus, and carbohydrate content, but all are amphiphilic. It can be found in the literature that the structure of the casein micelle is "hairy" due to the surface layer κ-casein which stabilizes the micelle [10]. Parts of caseins have regions that have hydrophilic and hydrophobic properties, which make it a surface-active molecule [9, 11].

Whey represents 85–95% of the milk volume and conteins approximately 20% of the protein in milk [12]. There are the two main types of whey, sweet and acid whey. Which type of whey will form depends upon the processing technique of separating the casein. The main differences in the processing technique between sweet and acid whey is the pH value, sweet whey at a pH value of 5.6 and acid at 4.5. Both mostly consist of water, the other ingredients according to their proportions are lactose, minerals, and whey proteins. Whey is a renewable raw material, but it is not suitable for disposal in the environment because its lactose ingredients need to be disposed of separately. The lactose component has a very high Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) [13]. Within the water body causes eutrophication due to the depletion of dissolved oxygen. Disposal in improper landfills can cause the build-up of compounds (salts) in the soil, reduce soil redox potential and acid whey can lower the pH level of the soil. Because of all the above, whey must be purified, and purification processes consume time, money, and energy. The use of whey as a biopolymer has the ultimative benefit of obtaining a renewable raw material and there is no need for its separate disposal.

In this research, the use of biobased polymers based on caseins and whey as a raw material for the production of materials used in the graphic and related industries will be presented by following the flow of material use in the production process. From paper used as a printing substrate or as a material for making packaging products, inks used in the printing process and adhesives used in postpress processes. By respecting the production process, the sustainability of the product can be easily increased, which can be shown by the analysis of the product life cycle [14]. In this way, increasing sustainability by using biobased polymers based on caseins and whey will get a numerical value and indicate the advantages that will be listed in this study.

PAPER COATINGS

The main constituents of paper are cellulose (40-50%), hemicelluloses (15-35%), and lignin (20-30%) [15, 16]. The species of wood determines the share of the mentioned components. In addition to fibers in the paper can be added fillers, sizing agents and chemicals. The main purpose of the filler is to fill the gap between the fibers to improve printability and print quality. Kaolin, talc, and calcium carbonate are commonly used. In addition to the mentioned paper may also contain retention aids, dyes, agents such strengthening agents, slime control agent, antifoaming agent etc.

Paper consists of porous and crystalline cellulose structure. The structure of the paper is composed of long-chain cellulose molecules in the crystalline state, which form microfibrils or porous cellulose structures. Amorphous regions regularly disrupting the crystalline structure. Another important structure in paper are amorphous areas that are hydrophilic and swell on contact with water or moisture from the air [17]. Such a property makes the amorphous structure flexible, while the porous areas are rigid and prevent the penetration of water or moisture, oxygen, and aromas. The fibers from the ambor region have ability to intertwine which brings the hydroxyl groups into a position where hydrogen bonds can be formed which contribute to sheet strength [18]. Hemicellulose chains distributed on the surface of the fiber can provide greater sheet stress because it has many hydrogen bonds. Due to the above, it can contribute to drawing more water into the fibers [19], but it has the property of soluble in water and is easily washed out of the fiber. On the other side when lignin is present on the fiber surface. it will block hydrogen bond formation resulting in lowering the strength of the resulting sheet [20].

Due to the porous and fiber-based structure of the surface paper or carboard and other properties that the packaging material must have, the mentioned materials must be treated by coatings. Coting by chemical composition can be based on petroleum-based polymers, biopolymers, or blends of polymeric and inorganic minerals [21, 22]. The components of the usual paper coating are pigments, binders, thickeners, and additives. The binder in the coating structure serves to bind the coating pigment to the base paper surface and the coating pigment particles together. It also helps to fill out voids between the coating pigments as the coating has been dewatered, participates in the modification of viscosity and water-retention while the coating is still fluid. Commonly used are synthetic binders as a styrene butadiene, and styrene acrylate or a polyvinyl acetate.

Coatings affect barrier properties against the permeation of fat, oil, water vapor or other gases. Common coatings petroleum-based polymers are applied by lamination or extrudion coated. Some of the conventional polymers used as water vapor barrier are high-density polyethylene HDPE, polypropylene PP, rubber latex and fluorocarbon, and some polymers used as an oxygen barrier are poly (vinyl alcohol) PVOH or ethylene vinyl alcohol EVOH. Coatings that contain petroleum-based polymers in the assembly affect the final stages of the life cycle of packaging products, ie their sustainable compaction in recyclability and biodegradability processes [23, 24].

Surface modifications of packaging materials deposition of fine layers of inorganic compounds (-SiO_x) can achieve barrier properties of exceptionally high quality. Unfortunately, making such materials has a few downsides. One of them is a complex technical process, which consists of two phases as follows vacuum deposition, plasma. The manufacturing process uses expensive materials and a lot of energy, which further increases the cost of production, but also affects the carbon footprint. Packaging materials with layers of inorganic compounds as well as the previously mentioned petroleum-based polymers are not biodegradable, and recycling processes are possible but not easily feasible. The cause of such behavior can be traced to their polymeric structures [25].

The natural polymers have the potential to replace synthetic paper coatings. Casein is used in the paper industry to produce high-quality glazed papers, enamel grades of paper and for fine halftone illustrations [26]. The role of casein in coatings is to balance the hydrophobic / hydrophilic properties, as it allows for better ink-binding and its adhesion to various substrates. Casein contributes to cross-linking as well as its less sustainable varints frequently used agents such as formaldehyde or dialdehyde. These compounds are used for crosslinking, their free amino groups bind to protein and give a threedimensional network. Lime can also be added to these agents. All the above adduce will contribute to better resistance to water. Acid casein in a moderate alkaline solution can be directly mixed with a water slurry of the pigments. The advantage of such a procedure is that it can obtain colored size and coatings [27]. Protein cross-linking can be achieved using physical procedures such as exposure to gamma irradiation and temperature [28].

In addition to the mentioned casein, caseinate coating can also be used. McMahon and Oommen 2008 was examined a sodium caseinate solution, the proteins formed a gel-like structure was forming a mesh with a strands or small agglomerates (Figure **1**) [29, 30]. Sodium caseinate have a linear and polar chemical structure which probably contributes lower oxygen permebilities. Described properties are usually associated with higher cohesive energy density and lower free volume [31]. The absence of calcium contributes to the translucent (non-milky) appearance of sodium casein solutions.

Coating based on sodium caseinate can contribute improves paper strength and ductility and reduce paper water vapor permeability. Further improve the impermeability to water and moisture on the sodium caseinate layer can be achieved by adding an

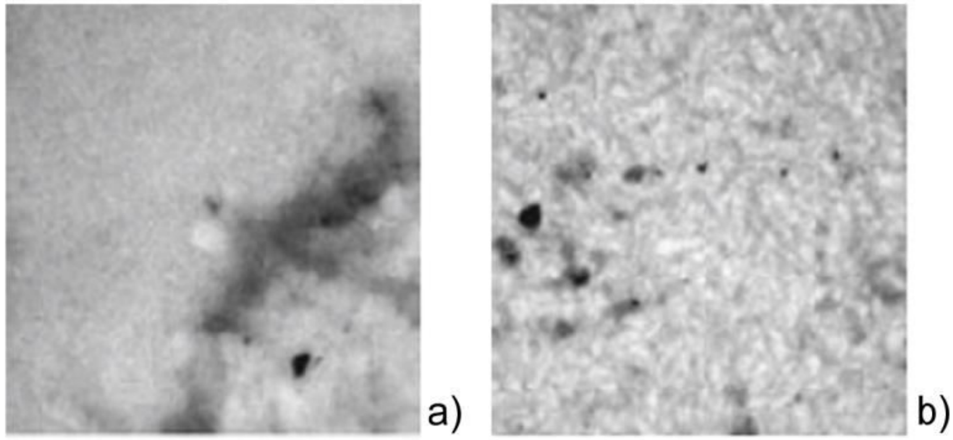

Figure 1: Snapshoot with transmission electron micrograph of field of view of sodium caseinate powder immobilization onto a parlodion-coated copper grid that was then stained with uranyl oxalate, rapidly frozen, and freeze-dried a) low magnification b) high magnification [29].

independent paraffin wax layer. In Sodium caseinate coating can be added additives such glycerol, mica and carnauba vax. In order to the multy-component coating have the best properties, the concentrations of the components should be adjusted so that it contains a higher proportion of wax over mica and a lower proportion of glycerol [32].

Whey protein is onother milk protein wich have use as coatin. By comparing properties natural polymer whey and frequently used petroleum-based polymers, whey proteins have excellent optical properties, excellent gloss and high transparency and good mechanical properties. Such properties could potentially reduce use of petroleum-based polymers like polypropylene (PP), polyvinyl chloride (PVC), and low-density polyethylene (LDPE) with which they are often compared [33, 34].

Whey protein an excellent barrier to oxygen even comparable to EVOH polymer in conditions at low or intermediate relative humidity [35]. Contributes to increasing oil resistance, reducing water vapor permeability (WVP) [36] and decreased the tensile strength [37]. The addition of additives as glycerol known plasticizer and protein to whey proteinadditionally reduces WVP. By monitoring WVP i their koncentration it can be determined that the mentioned substances have a synergistic effect on the water vapor permeability [38].

Authors Chan and Krochta describe coating the printing substrate with whey protein isolate (WPI) in order to reduction in oxygen permeability [39]. Said coating affects the surface properties of the paper making it more homogeneous and smoother. Such properties of the printing substrate significantly contribute to the visual effect regarding increase in gloss of paper. Chan and Krochta 2001 in the research i indicate a might replace commercial paperboard coatings such as polyvinyl alcohol and fluorocarbons with the mentioned coating due to its enumerated properties [36]. Denaturation WPI may affected the material properties. So for example it affects properties of water vapor barrier increased by about 35% and oxygen barrier properties increased by approximately 33% [41].

PRINTING INK

Eearly recorded history, at least thousands of years indicate much use of milk as a binder in milk artist paint. Caseinates have good emulsifying properties, so they have been used for many years as a good stabilizer and emulsifier in oil and latex painting paints. They are also used in water-based painting because solubility and ability to bind pigments. Their concentration in the mentioned paints is not significant, it makes 1 to 2%.

The properties of creating casein emulsions have is applied in printing inks. Emulsion polymerization influence on the environmental pollution, the purification processes and performance of the products. Soap-free polymerization emulsion allows no emulsifier migration during film formation, distribution particle is monodisperse size, and there is excellent shear stability [42]. Polymers with both hydrophilic and hydrophobic components can be used to obtain emulsifier-free polymer amphiphilic latexes. Such polymers have favorable properties as surfactants, due to their dual character they have different solubility of varied components. Ma J. at al 2015. was prepared amphiphilic copolymers, wich can be used to fabricate water-based ink binder. Casein-based emulsion was added to self-made amphiphilic copolymers AmBnCo using a polymerization free off emulsion process. Amphiphilic copolymers AmBnCo is stabilized the modified casein emulsions, created core – shell structure and moderate viscosity. Stability was shown via viscosity, where the viscosity of the emulsion without AmBnCo was higher than the emulsion with AmBnCo [43]. The described soap-free casein-based emulsion contribution is in increasing the sustainability of printing inks. The good side of Casein-based emulsion which finds its application in water-based ink. Such inks do not emit Volatile Organic Compounds (VOCs) as is characteristic of inks based on organic solvents and solvents due to their volatility. With mentioned modification casein-based inks do not contribute to the formation of smog type L.A. and are more environmentally friendly.

ADHESIVES

According to some sources, casein glues have been used from an early age since the days of the Egyptians and during the Middle Ages. In the nineteenth century comes from the increase of production through industrial production, the mentioned trend continues in the twentieth and twentie first century when new formulations of casein-based adhesives appear. It is made by heating sour milk or cheese by rinsing with water. In order for the isolate to be purer from whey concentrate with a higher protein content, non protein materials must be separated. The process of ultrafiltration of the concentrates whey purifies organic matter with the low molecular weight as lactose and fat, and inorganics, substances [44]. The ion exchange process further increases the protein content from 3O% -8O% to 90% -95%. Protein content after the first purification procedure depending on the degree of filtration. Alkali is then added, which leads to a reaction reassemble the micelle structure. The alkali can be introduced in an indirect manner witouth the water. The sodiumhydroxide can be replace with calcium hydroxide and convenient sodium salt of an acid whose calcium salt is relatively insoluble. In addition to all the above, its nonhygroscopic and nonreactivty with the lime of the casein must be provided. Examples of such specias are sodium oxalate, sodium citrate, sodium tartrate, sodium salicylate, sodium sulfite, sodium stannate or sodium fluoride. All of the above leads to an increase in the viscosity of the the resulting aggregate which assumes the properties of a paste.

Various additives can be added to the adhesives to obtain the desired product property. Recipes that are related to ancient times in their composition contain dissociating agents. Mentioned agents in adhesives limit the viscosity of the adhesive through lowered H-bonds between caseinates. Some of this group of compounds that are readily available have been long used like ammonia or urea [45]. In use are also lime or copper chloride. When thay are addition in the adhesive there is a significant crosslinking of casein molecules, which contributes increase to water-resistant glues. Great care should be taken in the amounts of additives added such as lime. If the maximum amount of lime is added, it will shorten the life of the product. In such cases it is better to combine adding copper chloride to obtain high water resistance but does not shorten the life of an adhesive and reduce the addition of lime. In this way, the service life of the product can be extended.

Another of the supplements is sodium silicate is significant due to it to prolong working life. Copper salts, the chlorinated phenols or their sodium salts are added to the adhesive to preserve the formation of molds or other microorganisms.

Additives that are related to the qualitative properties of the adhesive are tannate or alkali tannate, thay contribute to the increase of adhesion. To be achieving water resistant and ice-proof properties metal salts can be added. Such an adhesive is used in a bottle label adhesive [8]. With the mentioned a bottle label adhesive adhesive satisfies must condition another important property. Such labels must be easily detachable on the beginning process of washing the bottle, and caseine adhesive has the property of easy separation in an aqueous medium [46, 47]. Casein glues can be used in bonding paper.

Another ingredient in milk are whey proteins, thay can be used too as a raw material for making adhesives. Whey proteins can be categorized into acid whey with pH below 5.0, and sweet whey with pH around 6 or higher [48]. Wheys proteins has not been used since earlier history because thay are generally composed of compact globular proteins with lower molecular weight and multiple components. No matter of the specific properties mentioned abowe, whey proteins have some positive properties as readily soluble in water, able to form a homogeneous solution, it has free hydroxyl groups and residual amino group [49]. In addition to the mentioned globular structures whey proteins could be modified into relatively linear structures [50].

The first mentions of using whey protein to make adhesives are related to the middle of the last century. Since that time, the mentioned raw material has been widely used due to its ability to combine with synthetic copolymers. In this way, part of the raw material is an adhesive of renewable origin, which contributes to increasing the sustainability of the product and reducing the carbon footprint. Syntetic adhesives contribute to the carbon footprint by choosing raw materials that are not renewable cross-section. Synthetic additives such as poly (vinyl acetate) (PVAc) and poly (vinyl alcohol) (PVA) are usually obtained from the same starting monomer vinyl acetate monomer (VAM). Raw materials witch is produced from fossil resources or crude oil such as ethylene and acetic acid to make the initial monomer VAM. VAM monomers can be obtained by using bioethanol as a renewable resource. Renewable sources used in its production are the most commonare sugar cane, corn, or preferably straw and other non-food parts of plants. On this way is possible to obtain an adhesive which is completely based on a renewable raw material and which reduces the carbon footprint. Many authors have studied biodegradbility including Matsumura 2003 [51]. If the adhesive is made from the listed renewable resources, its biodegradable is possible. In order for biodegradability of PVA to occur, several conditions must be met as availability of water and the occurrence of biotic or abiotic structuresthan wich can be interact with the polymer surface. Another determining factor of biodegradation is the existence of microbial organisms that can assimilate the PVA molecule.

One of the important parameters in using of adhesive is the durability of the product, the previously mentioned additives do not contribute to the durability of the adhesive. In order to produce a sustainable product, it is also important to optimize durability. The use of PVAc and PVa is recommended for products whose durability does not have to be great because after some time it turns into a gel. For products with a longer shelf life, polymerized whey protein with polyvinyl pyrrolidone (PVP) is recommended. In addition to the ability to formfairly stable complexes and association compounds and the unique combination of extraordinaryphysical and chemical properties as nontoxic, and biocompatible polymer, chemically inert, pH-stable and temperature-resistant, which puts it is high on the list of desirable additives [52, 53]. PVP was designed in the laboratory in 1938, Walter Reppe was responsible for its favorable characteristics. A pplications PVP is in various products besides adhesives like paper, coatings and inks, lithography and photography.

The low price and good availability of sucrose has made it a good alternative to additives in whey protein adhesives. Sucrose has the property of stabilizing protein under elevated temperature conditions [54]. The complementary structure of sucrose and paper contributes to the bonding strength. Hydrogen bonding links hydroxyl groups chain molecules sucrose with hydroxyl groups of paper [55, 56].

The growth in the use of glasses has left its impact in this area as well, nanoparticles have been added in polyvinyl acetate (PVAC) and polyvinyl alcohol (PVA). Such research was conducted by Zhao *et al*. with nano-CaCO3, PVAC and PVa was blended with whey proteins, which contributed bonding performances of whey protein / PMDI adhesives was improved [57].

The thiol group in α-La protein under mild denaturing conditions contributes to better heat stability and molten globule state [58]. Mentioned thiol groups are also found in the β-Lg configuration, witch contains in addition to one thiol group and two disulphide bonds. Significance α-La and β-Lg configuration come's from presence of the thiol group and the disulphide bond which results in excellent gelation property and are significantly affected on the properties of the adhesive. The chemical processes that lead to the gelation process take place under elevated temperature conditions, where interchange a thiol-disulphide [59].

Whay proteins in addition to all the above tlisted are rich in lysyl residues. Lysyl residues have very active ε-amino groups to which crosslinkers can be attached. An example of such crosslinking is crosslinking with glutaraldehyde (GTA) [60].

CONCLUSION

Synthetic petroleum-based materials have for many years dominated the graphic and related industries. In recent years, in conversations with commercialists who sell printing materials and packaging products, one can hear the concerns of customers about the impact environment and the desire to increase the sustainability of graphic products and production. Environmentally safe bio-resourced and renewable polymers are increasingly used especially in products related to food or pharmaceutical products where product safety is a very important factor.

One of the negative factors influencing the increase in milk protein use is cost. The demands for milk protein increase in the food industry due to its high nutritional value, but lot of food products are thrown on the market because their expiration date for safe use has expired. It is certainly more sustainable to use such products as a raw material to produce materials in the printing industry. Further wind in the back development and use products on the base milk proteins gives the development of modern technology and the chemistry with the help of which new formulations can be designed. new forumulation have the desired properties with undisputed safety in relation to people and the environment. All of the above milk proteins will have a niche in the future in the market of the graphic and accompanying industries.

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