Environment. Technology. Resources. Rezekne, Latvia
Proceedings of the 15th International Scientific and Practical Conference. Volume III, 358-362

Laser radiation made hydrophobic surface on stainless steel for food industry, a review

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Abstract. **Main requirement in food processing industry is providing a food safety through all the production cycle. One of many procedures that guarantee food safety is cleanliness of surfaces that are in contact with food or its raw materials. Surface cleanliness could be achieved in different ways, either by regular washing with clean water and detergents or by creating surfaces, that repel water or other residues. It is important, because remaining water with residues create conditions for growth of unwanted microflora.**

As classic, or active, cleaning method of washing with clean water and detergents require a lot of resources and energy. But nowadays more and more self cleaning, passive, methods are used, such as hydrophobic surfaces. These surfaces are made with in different ways, where most common are water reppeling coatings, for example – wax. But there are other methods, such as laser radiation treatment, that can create hydrophobic surface on required material, such as stainless steel, which is most common used material in food processing.

There are studies that show effectivnes of laser radiation created hydrophobic surface for water repelling, but unfortunately, there are no researches found, that could provide information of such surface interaction with milk. As milk by itself is water emulsion with different nutrients, its most favourable environment for microbiological growth. By examining and analyzing different scientific articles, that are linked to topic of hydrophobic surface usage in food industry, it was concluded, that laser radiation made hydrophobic surfaces on stainless steel could have large potential. Especially in dairy industry, where such surface treatment could decrease risks of microflora growth and save resources and energy that are required for active washing process.

Keywords: Hydrophobic surface, laser treatment, milk, stainless steel .

I. INTRODUCTION

Food is the basis of human health and longevity, where the main role is played by its quality and safety. Throughout human history, various methods have been discovered and tested to improve the quality and safety of products, which are ultimately successfully applied in practice. At one time, such revolutionary processes as pasteurization and sterilization are now a given. With the advent of new materials and types of packaging, the quality and safety of products became even better, where we also should not forget about the development of the concept and requirements of hygiene. This is one of the reasons why modern human is able to live a longer life than his ancient ancestors [1].

Nowadays, food processing and hygiene technologies are developing further, but there is still a kind of stagnation of innovations or revolutionary ideas, since the basic technologies and processes almost fully satisfy modern needs. The main vector of development at the moment is related to environmental protection, saving energy and materials, as well as the movement for a healthier lifestyle and alternative food products. This movement creates new challenges for science and industry, since some basic technologies of food production and hygiene cannot fully solve them, and sometimes even go against them [2], [3].

Of the many potential directions in the development of food safety and quality, the use of various types of surfaces that repel water or oil shows promise. One of the most famous examples are anti-stick surfaces for frying pans and waffle irons. These surfaces actually help save cooking oil and detergents for cleaning burnt marks. Another example is the wax coating on paper cups and cardboard tetra packs, which prevent the liquid product from wetting the packaging. Thus, for the transportation and storage of liquid products, more environmentally friendly and lightweight types of packaging can be used [4].

But still, these properties are obtained by applying one material to another, which in turn creates a potential threat of foreign substances or particles entering food products. As a solution to this problem, new methods of obtaining repellent surfaces are being developed, for example, laser processing, where the structure of the base material performs the necessary functions. In this case, such surfaces may be suitable for the dairy industry, where the

Print ISSN 1691-5402
Online ISSN 2256-070X
https://doi.org/10.17770/etr2024vol3.8172

issue of food safety and hygiene is at a special level, since milk is one of the most favourable environments for the development of microflora, and also, milk is very sensitive to contaminants that can negatively affect on its organoleptic properties [5].

II. HYDROPHOBIC SURFACES IN FOOD INDUSTRY

Main risk factor in dairy processing is biofilm creation on stainless steel surfaces. This biofilm is created by bacteria and milk residue, that could be resistant to most cleaning protocols and thermal processing. Also, biofilm decrease heat transfer, where even 0,05 mm thick biofilm layer results in 30% heat transfer decrease. Finally, it's proven that biofilm also can cause surface corrosion. All these milk biofilm effects not only increase risk of dairy product contamination and quality loss, but also could lead to ineffective work of equipment or even damage it. Considering these factors, solutions of removing or at least minimizing biofilm effects for dairy industry are needed. In that case, article authors have conducted experiment, where 4 different materials where applied on stainless steel AISI 316, such as: Ni-P-PTFE, AMC-18, Dursan, Lectrofluor-641. Ni-P-PTFE coating showed most promising results, due to high resistance to biofilm formation and other residue attachment. Comparing to control example (clean AISI 316), new coating decreased surface roughness by 43% and increased contact angle by 2-3 times, showing that Ni-P-PTFE coated example is more hydrophobic. Unfortunately, these tests were condemned only under limited lab conditions, and there were no further researches found, that could show Ni-P-PTFE coating durability in real life conditions and its interaction with milk itself [6].

There is other method that helps to prevent dairy product contamination with biofilm forming bacteria, by using superhydriphobic wax surfaces. Tests have proven that even under similar conditions as in dairy factory, where continuous flow of milk and cleaning fluids are present, biofilm development was cut up to 99%. Also, paraffin/fluorinated wax coating has shown no negative effects on milk quality, in comparison to other technologies, that were available up to 2019 [7].

As a solution to minimize bacterial cross contamination where leafy vegetables were in contact with stainless steel surfaces, nickel- nanodiamond nanocomposite film was created on AISI 304 stainless steel. This coating has shown good superhydrophobic properties with static water contact angle of 156.3 ± 1.9° and durability to cleaning process [8].

Quite a number of articles where found where food safe hydrophobic coatings were used for packaging in order to minimize liquid food waste. It is very important problem nowadays not only due to waste of products as a resource, but food residue itself creates good environment for pathogenic bacteria and fungus evolving and spreading. Also, dirty used package usually is not properly recycled, as it requires resources and energy for cleaning [9]. In most cases, natural wax and ethanol solutions were sprayed on most common used types of packaging. Insect waxes such as Shellac and Beeswax were proven as a robust coating on paper packaging, where 145° contact angle was achieved [10]. Mixture of beeswax and coffee lignin creates coating with more than 150° contact angle and stability to long time heating and flushing [11]. Microcrystalline or paraffin wax coating gives 158° contact angle, is resistant to pressure washing and corrosive water based solutions. Can be applied on substrates as PET, PE and glass where shows great anti adhesive properties to products such as: honey, cola and dairy products [12]. Food grade candelilla and rice bran wax shows similar contact angle and resistance results. It also can be applied on materials such as: aluminium foil, paper, PTFE, PP and glass [13]. Also soybean wax coating has similar properties, with 159° contact angle, but it starts to lose its superhydrophobic properties if it is hated above 50°C, that makes it unsuitable for use with heated liquid products [14].

Other non biological coatings were tested too, such as paraffin wax combined with clay minerals or multiwalled carbon nanotubes. If paraffin-clay performs similarly to other bio-wax coatings [15], multiwalled carbon nanotubes have even better properties, where contact angle is 167°. Coating is extremely durable, resisting intensive water jetting, immersion in corrosive liquids and temperatures up to 390°C, which is far more extreme conditions, that are commonly used in liquid food production, but unfortunately, it is not known if such coating is safe for health in long term [16].

Overall, more and more hydrophobic coatings are used not only for food packaging, but for food itself, creating eatable protective coating. Most of these coatings are made from bio-wax for paper packaging, which in some cases is a good alternative to PS and PP packaging. Except minimisation of food waste and protecting materials from wetting, hydrophobic surfaces have proven its effectiveness against microflora growth and corrosion of metals. Other, non natural coatings are developed too, but not all are usable due to costliness, technological complicity or food safety concerns. Use of laser texturing for creating hydrophobic surface on main material, without using any coatings, is quite promising [17].

III. HYDROPHOBIC SURFACES CREATED BY LASER RADIATION

Laser technologies have opened wide spectrum of possibilities, that in some cases were not possible before. In case of laser texturing, process, where laser beam creates precise surface texture by melting or evaporating top layer of processed material in programmed pattern, makes possible to create surfaces with different properties. Creation and examination of hydrophobic surfaces on different materials using laser radiation is quite popular for many researchers nowadays, where stainless steel is commonly used due its wide usage. As laser texturing is only a surface modification process, it does not require high power laser sources [18], [19], [20], [21].

Using 800nm Regenerative/Multi-pass Ti: sapphire laser system with 130fs pulse duration and 1kHz repetition rate it is possible to create hydrophobic surface on stainless steel with 166.3° contact angle and 4.2° sliding angle. Increasing laser fluencies (from 0,1 to 2,5 J/cm^2), contact angle also increased (from 150 to 166.3°) [22]. In other case, a 1032 nm femtosecond laser with

310 fs pulses, 5 W average power output and a circular polarisation for texture creation was used. Main goal was to achieve large area surface treatment with single step process with high speed (1 m/s) and pulse frequency (500 kHz) [23]. Similar research authors experimented with different laser fluencies (from 178 to 1143 J/cm^2) achieving surface with 164° ± 5° contact angle that saves its hydrophobic properties for 30 days after treatment [24]. Finally, another femtosecond laser was used in other one research, where authors used achieved 156° contact angle on AISI 304 stainless steel [25].

Nd:YAG laser with wavelengths of 532 nm and 1064 nm also could be used for stainless steel microtexturing. Even more, a comparative research was made for creating superhydrophobic surfaces in different medias. Since air or inert gas media is most commonly used, water media provides better heat sinking due to its high heat capacity, makes possible to control generated temperature gradients and most important – redeposition of ablated particles is prevented [26].

Nanosecond lasers could be used for stainless steel texturing too. For example, 1064 nm nanosecond fiber laser with 20 kHz pulse rate, 100 ns pulse duration and 1mJ pulse energy was used to create surface with maximum contact angle of 153.3°. It was achieved by creation of microstructured surface pitch of 110 µm with 14 W laser power [27]. Very detailed review article theoretically proves effectiveness of superhydrophobic surface creation on stainless steel with different wavelength nanosecond lasers [28].

Regardless of stainless steel high resistance to corrosion, under some circumstances it still can deteriorate. As hydrophobic surfaces repel water, this factor by itself is a good way to minimize possibility of corrosion process. Several researches have been made to create hydrophobic surfaces on different metals by laser treatment, in order to fight with corrosion. In all cases, research authors have achieved good results to create self cleaning superhydrophobic surfaces on stainless steel using different laser types [29], [30], [31], [32].

From microbiological point of view, it is proven, that laser made hydrophobic surface on stainless steel can reduce growth of most common bacteria by 99.8% for *E. coli* and 79,1% for *S.aureus*. Antibacterial effect is achieved due to hydrophobic surface that repels water with residues, that is the main media for bacterial growth [33].

In most cases researchers focused their attention only to surface ability to repel water, but there are different kind of oils, fats, alcohols or their mixtures, that in some situations have to be repelled too. To achieve this effect, an omniphobic surface have to be created. Quite noticeable is article, where authors managed to create superomnyphobic surfaces on different kind of materials, including stainless steel 304, 316 and 340, that repels both water and n-hexadecane. Use of 10.2 µm CO2 laser engraver, proves, that such surfaces could be created even with much simpler equipment. Unfortunately this surface has shown poor mechanical durability, but still can be used in cases, where solid particles are not present [34]. Other way of creating superomnyphobic surface on stainless steel was made by using nanosecond laser on AISI 304 stainless steel and treating surface with aqueous solution of perfluorooctanoic acid, superomnyphobic surface was created, that repels different substances such as: water, hexadecane, peanut oil and glycerol (with contact angles 165.77°, 152.83°, 155.24° and 155.09°). This surface has self cleaning effect and good wear resistance, that is guaranteed up to two months under natural conditions [35].

TABLE I. COMPARISON OF DIFFERENT LASER SOURCES FOR ACHIEVING SUPERHYDROPHOBIC SURFACE ON STAINLESS STEEL.

Laser type	Wavelength | spot size	Power density or pulse power	Pulse | rate | scan speed	Water contact angle	Source nr.
NIR Ytterbium Fiber Laser system	1060 nm | 30 µm	n/a	n/a | n/a | 5000 mm/s	>150°	[32]
YLP-ST20E fiber laser	1061 nm | 50 µm	7643 W/mm2	100 ns | 20 kHz | n/a	>150°	[29]
Nd:YAG laser	1064 nm | n/a	31 J/cm2	95 ns | 1 kHz | n/a	153°	[37]
Nanosecond pulsed fiber laser	1064 nm | 15 um	1 mJ	100 ns | 20 kHz | n/a	153.2°	[27]
Yb:YAG DLIP laser setup	1030 nm | 60 µm	0.05 & 0.1 J/cm2	8 ps | 100 kHz | 100 mm/s	154 ± 3°	[33]
UV nanosecond laser	n/a | 30.0 µm	8.14 J/cm2	n/a | n/a | 20 mm/s	160 ± 5°	[31]
Regenerative/Multi-pass Ti: sapphire laser	800nm | LIPSS - 0.5 µm	0.08 & 0.2 J/cm2	130 fs | 1 kHz | n/a	166.3°	[22]
Nd:YAG pulsed laser (LPKF, OK DP10)	1064 nm | n/a	86.45 J/cm2	40 ns | 25 kHz | n/a	168 ± 3.0°	[36]
CO_2 laser engraver	10.2 µm | n/a	120 W	n/a | n/a | 20 mm/s	168°	[34]

IV.CONCLUSIONS

Main inspiration of self cleaning or "lotus effect" comes from nature, where plants and animals have developed ability to repel water for various survival reasons. That is why, idea of self cleaning, water repelling surface is always actual for human daily life. From this research of current situation in field of using hydrophobic surfaces in food industry, it is clear, that a lot methods exist for achieving water or other substance repelling effect on most of materials. Laser texturing on stainless steel, most common used material in food processing, provides promising results for future researches and implementation of new technologies. This surface treatment could be done by large variety of laser sources and their work parameters, but the key for achieving superhydrophobic effect is a texture of surface itself. It would be desirable to create a template of an "almost perfect" 3 dimensional texture map of the surface, that provides best superhydrophobic effect.

As most researches were carried out to create water repelling surface, our aim for future researches is to create milk repelling surface on stainless steel, by using available laser setups in order to find new ways making dairy industry more safe and efficient.

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