REVIEW OF FOOD TOXICOLOGICAL ISSUES ASSOCIATED IN RUBBER PRODUCTS

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Abstract: Over the centuries, rubber latex gained its popularity in machinery application due to its unique thermal properties, high elasticity and excellent impact resistance. It is widely accepted in food industry as rubber has good resistance to chemicals, including acids, alkalis and salts. For instance, rubber components comprise of couplings, shields, dust covers, gaskets and seals exist as group or standalone component in food manufacturing equipments or machinery. Even though most of the rubber based products in food industry fulfil the requirements of Food and Drug Administration (FDA), however, the presence of trace amount of chemicals upon the preceding processing of rubber might accidentally contaminate to the food products. The contamination that happened might caused changes in food quality in term of taste, smell or even visual appearance. Therefore, this paper aims to review some of the manufacturing process of natural rubber products and to understand the possibility of extractable and leachable contaminated food products. An overview of potential toxicological problems will be discussed and the finding will be summarized in this paper.

Keywords: rubber products, contamination, food quality, toxicological problems

INTRODUCTION

The industrialization of food products is getting common as to meet the growing urban demand. Food production with shorter processing time and mass production are getting easier by emerging technology. There are some pros and cons of industrialized food production. In example, good quality food can be easily produced from the factory and the refine food products usually visually look better and have long shelf life (Ahvenainen, 1996). However, some of the industrialized food might threaten our health due to over processing. The food's nutrient might be loss during the processing and a lot of food additive are added. Besides that, food contaminants might be happened anytime during the process.

Recent year, there are a lot of food contamination issues and the most noteworthy incidents would be the contaminated protein, melamine is being used in milk powder manufacturing in China (Xin, 2008) that lead to 300,000 victims with six infants mortality. This case has revealed that the economic gain is most important for a manufacturer and this act had placed people life at stake. The manufacturers pledge to provide high quality products with low selling price. However, in order to reduce processing cost, some might not using food grade equipment and produce food products through deliberate adulteration (Collins, 1993) to lower their capital. Besides that, there is another case related to black licorice products that usually consumed by kids. All the products were recalled on year 2012 due to the high lead contamination (Aleccia, 2013). In addition, there are several example of food contamination happened on 2013, such as almond cakes with coliform bacteria (Jens, 2013), milk with aflatoxins (2013a), vegetables with rat poison (2013b), and so on. The contamination might happen anytime in food processing easily without any precaution. From the farm till finish products, including transfer process, heating and cooling process or even the packaging itself might contaminate the food products.

In general, contamination means that it happened without any intention added to food and it could be happened more than one stage in the process, which all the food contact materials (FCM) possible to have

some chemicals migration to the food products. The food toxicological issues and food borne illness might happen when someone eaten too much of the contaminated food products or the food contamination level is too high. All the mentioned food contamination cases had seriously affected the public confident on processed food.

RUBBER

In a lot of food processing industry, rubber products are widely being in used, such as gaskets, conveyor belt, hose or rubber seal. Rubber is normally chosen to be used because of its process ability, material properties and price. It is useful in food processing equipment because of its elasticity and its wide application. The uniqueness of natural rubber properties has once drawn a large demand worldwide. As rubber is a bio-origin material, it shared the common properties of other organic materials, which are low density, good insulator and low permeability of liquid. At the time without the available of synthetic rubber alternative, all the wiring coating was made by rubber. Even a warship would consisted up to 20,000 rubber part (2011).

For instance, the rubber still widely applied in most of the manufacturing industry. Majorities of the rubber demands are from automotive tyre manufacturing and there is uncountable sum of rubber being used as processing aids and materials in contact with food in food processing industry (Faille, 2009). In example, the main uses of rubber in conveyor belts, seals and tubing are considered indirect food additive as it came into contact with food. The ability of rubber to resistant to oil, gas, light, and even acids, make it frequently being used as gasket in food processing plants. Basically, rubber can be used in food transportation, food handling, food netting, pumping systems, general seal and pipe-work components.

As the popularity of rubber remain high and the understanding in chemistry increase, many research studies had been carried out to determine food contaminants due to rubber products. There is increasing number of reports showed that the vulcanization and cross linking process in rubber might have induced some chemical constituents that easily migrate to food products. The chemical constituents from the processing of rubber products might be harmful to human's health and caused food toxicological happened. One of the example is from the research paper written by Fajen (1979), he revealed that N-Nitrosamine exists in rubber products has carcinogen properties, but the enforcement to change the sulfur, accelerator, and filler ingredient for teats and soothers only established on year 1995. The rubber infant products have been strictly managed since then, but only Food and Drug Administration (FDA) legislation is in place and covers the use of rubber in food contact applications, while the rest is mostly focus on food safety. The other food safety agencies such as U.S. Pharmacopeial, European Food Safety Authority (EFSA) and European Union (EU) always ensure that manufacturers followed the rules and regulation and only food grade chemicals or material is allowed to manufacture the food grade products. Once there is chemicals tainted food products found, it would be remove from shelves and recall immediately.

Rubber compounding

The original form of natural rubber do not usually contained high amount of any contaminants; but the addition of necessarily chemicals in rubber compounding to crosslink and vulcanized the rubber particles will caused the contaminants exist in rubber products. The main component in compounding formulation is sulphur, which normally acted as cross-linker, while zinc oxides functioned as activators. The vulcanization processes of rubber able to strengthen it to a more durable product.

Due to the long curing time of rubber, addition of accelerator, in example, urotropine, dithiocarbamate or thiuram is normally used in combination with sulphur and zinc oxide to speed up the rubber maturation time. During heating, formaldehyde might be released from urotropine, while the use of any derivative of secondary amines will caused nitrosating to occur, as they are the precursors of N-Nitrosamine (Spiegelhalder, 1982). Besides this, some bacteria able to catalyze N-nitrosation reaction and that might further increase the N-nitrosamine content in rubber products (Michael, 1996). However, the N-Nitrosamine content can be reduced with the change of accelerator materials to 'safe' amino components, as mentioned by Wacker (1987). By the elimination of nitrosating agents, the nitrosamine level is able to reduce drastically in rubber products (Fishbein, 1983). Nitrosamines content is usually detected by the use of Gas Chromatography (GC) analyzer, but the preparation method and sample rubber have to take into consideration as the level of nitrosamines might be differ in different area of rubber products.

Besides those chemicals that must be used to elevate rubber properties in usual manufacturing practise, furnace carbon black, a type of filler that currently being used at high percentage in natural rubber products for economy gain purpose. Carbon black itself is a group 2B carcinogen and will lead to lung cancer (Kuempel, 2010). However, during liquid transfer, especially for edible oil and milk contact application, the filler content has to be lower than 10% according to FDA legislation (Regulatory, 2013). Even though the filler content is lower, liquid food might be more aggressive compare to solid and would interact with the furnace carbon black in

rubber products. From the info, carbon black itself is a nitrosating agent which increased the nitrosamine content in rubber products (1994b). The replacement of carbon black could be calcium carbonate or silica, which possible to reduce the nitrosamine content. However, as to improve the economic gain, high filler content might be dose into products, the filler in rubber might cause some implications to the food products through food processing equipment.

Besides those essential chemicals mentioned above, some releasing agents, such as calcium carbonate, potassium stearate or silicone based lubricants always need to be used to reduce the tackiness of rubber products. These chemicals are not bonded chemically to rubber product which the chemicals migration might occur easily at the later stage. There are high amount of hydrocarbons in the chemicals that readily contaminate food (Grob, 1991). With prolonged duration of contact with high surface area of aggressive foodstuffs at high temperature, it is possible for food contamination to happen easily.

Sometimes, addition of plasticiser would help to improve the durability of natural rubber products, but the maximum requirements for plasticiser that can be used in rubber product or other types of elastomers are up to 30% (Regulatory, 2013), which might be caused phthalates contamination in food. At high percentage of plasticizers, phthalates could leached off the products and migrate to food surface easily. The consumption of phthalates will further lead to rodent liver carcinogen (Cao, 2010) and reproductive system disruption (Cherif Lahimer, 2013). Fatty food is one of the major sources that prone to phthalates exposure as phthalates are lipophilic, but yet the regulation of plasticiser usage vary from country to country (Cao, 2010), which lead to high phthalates contamination in food products. Other types of plasticiser, namely polychlorinated biphenyls that are banned since 1970s still found on animal feed contamination and discovered through recent cases happened in Belgium (Adrian, 2008).

In the formulation of rubber compounding, from the vulcanisation agents, activator, accelerator, plasticiser, filler, anti-tack agent or antioxidant, and stabilizer (Scott, 1988), all these compounds in rubber products might be potential toxicological issues when use as FCM. In the case of application of rubber products as a FCM, all chemical extraction test have to conform to the standard set by FDA, but those products that do not export to united state might not required to pass the standard. This means that there is a high possibility of chemicals migration from rubber products to food at many places.

Indirect food additive

There is a list of permitted food additive and the food grade raw materials for manufacturing process approved by FDA. Those materials that are inherently safe to use would be classified as generally recognised as safe (GRAS) materials (Noah, 1998) and those permitted food additive are based on analytical limit of detection. However, asbestos fiber, phenyl-β-naphthylamine and some commonly understanding as hazardous materials is permitted for indirect food additives in polymers (Regulatory, 2013). The lists on FDA website might be misleading manufacturer that the materials are safe to be use. Manufacturers might follow FDA's permitted ingredient and formulation to product food grade rubber products but still fail the inspection of extracted chemicals from the products. As rubber is permeable and high porosity materials (Han, 1999), there is a high possibility for the chemicals migration to food happened. The usual chemical contamination by the rubber products, such as polycyclic aromatic hydrocarbon (PAH) (Eir ķur, 2009), nitrosamine (Straif, 2000), or phthalate (Vermeulen, 2005), heavily depends on the chemical added to rubber products and the processing method.

By referring to FDA, the usual limitation of the content of carbon black is not to exceed 15%, however, due to the direct heating process, there is high amount of PAH in carbon black (Charles, 1968) readily migrate to any contact surface. In comparison of various report by Thitiworn (2010), natural rubber ribbed smoked sheet (RSS) factory consists of higher PAH contents compared to carbon black factory, which means that PAH might be present in RSS products as well. RSS is one of the raw natural rubbers that are often turned into rubber sheet by calendaring process. The other solid form of natural rubber product, such as brown crepe is contaminated with dirt and poor quality; while block rubber that need to fulfil the technical specification will employed infra red radiation drying or hot air convective drying, this drying process will have less PAH contents compared to smoke process. Even though block rubber is technical specification rubber (Setyamidjaja, 1993), it is more likely to be used in tyre manufacturing instead of food grade rubber products.

In previous study of Sheftel (2000), he found out the report on the migration of PAH from rubber products into foodstuffs indeed happened. Some analytical tools will able to reveal the contamination happened in food products. GC analytical instrument as one of the most frequent used detectors for food contaminants (Sannino, 2013). As the development of analytical technology going on and the analytical technique is getting more precise, the toxicological assessment of each additive material should be updated and the extraction limit in food test should be renewed.

In short, the contaminations in food products can be prevented by eliminate the use of hazardous chemicals. However, most of the time, the conventional analytical techniques is tested for food safety, but not for toxicological assessment. Even though the contaminants are detected, traceability back to the area of contamination to improve the condition might take some time. This is due to some contaminants might be the complication of a series of process and the traceability process seem impossible.

CONTAMINATION

In most of the time, rubber is not used as the main component in food processing equipments. The preferred materials for the equipments are normally carbon steel, stainless steel, aluminium and plastics as they are easy to clean and sanitize. Metals are able to resist impact damage, while rubber prone to deteriorate fast under hot environment. The chance of bacterial contamination in rubber products are much higher compared to metal as the cracked surface on rubber might accumulate a lot of bacteria (LeClercq-Perlat, 1994). Besides that, as rubber is a hydrophobic material, bacteria prone to attach itself to more hydrophobic materials (Sinde, 2000).

In the milking industry, rubber hoses are being used for milk transfer, so the high contact area of milk with the hose might cause contamination to happen. As the bacteria deposited inside the rubber hoses, cleaning failure will lead to bacterial contamination in raw milk. Some of the washing procedure as mentioned by Sinde (2000) has no effects towards certain bacteria and thus biofilm might form inside rubber tubing (Pilar, 2005). For this reason, the rubber hoses have to be replaced by a fix schedule to prevent fungal toxins.

Besides of bacterial contamination, migration of chemicals is closely relate to contact time, area of contact, type of packaging, and processing temperature. Normally packaging has the longest contact time; however, in this case, rubber is not suitable to be used as packaging materials. Thus, the longest contact time of rubber products with food would be in fermentation industry or beer brewing industry; while the highest contact area would be the use of rubber hose for milk transferring process or at the heat exchange gasket prior fermentation (Sidwell, 2000). Due to long contact hours and large contact area, there is a high possibility of PAH, nitrosamine or phthalate transfer to food products. As the contact time of the food products with the rubber getting longer, more chemical migration might be happened.

Some of the rubber products produced by using mould extrusion process might have used some solvents during their cleaning stage. From Kromhout's study, he found out that there is 56% of tasks in rubber manufacturing industry have to use solvent directly, which included cleaning process (1994). The solvent residue on equipments' surface might be transfer to rubber product and further contaminated food products as mentioned by Martin (2013) in his research study. This part is unpredictable and only able to be found out after the rubber product is produced.

Most of the time, the same rubber processing equipment is used for food grade and industrial grade. The production line will have to be cleaned thoroughly before manufactured the food grade products unless there is a specific line for food grade products. Thus, there is a possibility that the failure in cleaning caused non food grade chemicals seep into food grade rubber products (2003). In the case of coloured rubber products, the pigment from the previous products might stain the processing equipment and lead to poor cleaning process. Some of the coloured rubber products might be removed especially when in contact with acidic, alcoholic, mineral oil or fatty products (Sidwell, 2000). From all the statements above, we can clearly see that there is a high possibility that rubber processing chemicals migrate to food in the food processing industry. A details review done by Forrest has described how chemicals will migrate from rubber to food (Forrest, 2007).

Food processing

Besides the rubber processing part, there are several pathways for the contaminants to reach food products in food processing industry. Contaminants can happen anytime during the manufacturing process, transportation process, due to the environment or storage condition. In the food preparation by baking, grilling, smoking or frying, the process might cause an increase in the PAH or Nitrosamine content. In certain case where meat netting is required to keep the food textured, the elastic rubber netting with trace amount of nitrosamine possibly migrate to cured meats (Sen, 1987). Those nitrosamine that found migrated to meat products was due to the reaction of nitrite in meat and amine in rubber but not necessary carcinogenic to human (Sen, 1988). As the food is heated, the composition inside food will disintegrate and react to heat and rubber, thus, more contaminants will migrate to the food. U.S. Department of Agriculture (USDA) has take action since 1990 to discontinue the use of meat netting (Anonymous, 1994a). In China, the food grade rubber products are tested for volatile organic content, solubility of organic content and heavy metal test (2012). However, due to too much of black market high value food products and products sold without certification, there are a lots of chemicals contamination in the food products (Huang, 2010). However, for other common food additive that do not impose any health threat to human, reasonable

consumption of process food with additive content is acceptable (Lowik, 1996).

Others

The usage of synthetic rubber is quite popular in food industry as different rubber will exhibit their unique properties. Silicone rubber has the advantage of stable and low toxicity makes it suitable to be used as FCM, while other synthetic rubbers, such as nitrile, chloroprene, and butadiene consists of carcinogenic compound, 1,3- butadiene, so they are not suitable for food application. Styrene-butadiene rubber is relatively stable compare to its monomer, so it is suitable for food grade rubber products.

Besides that, the processing machinery needed to use lubricant to reduce the processes' friction. In common lubricants, it would contain high amount of hydrocarbon, which is potential source of food contamination (Grob, 1991). The water source of food processing is equally important, some of the small manufacturers would use old plastic container to store water and caused the water used to process food might contents chemical constituents like glyoxal and ethylene glycol (Huang, 2010). In addition, the excessive preservation of raw meat might cause food toxicity (Shtenberg, 1970) to happen and a potential treat to human's liver, kidney and digestive system.

CONCLUSIONS

The usage certain compounding chemicals for rubber products in food processing has been strictly enforced, however, due to different regulations in different countries, the condition of manufacture process might not well control. There is a high possibility of potential food contaminants from rubber products and other source. Besides that, the indirect food additive lists as mentioned by FDA should be revised. The tolerance of food additive might be causing manufacturing of highly contaminated food. The control of food quality should be strictly monitored to prevent any toxicological cases happen. In future studies, details understanding of the relation of food contaminants with all kind of illness should be study in depth, the long term effect to human health should be justified as well.

NOMENCLATURE

Subscripts

FCM Food contact materials
FDA Food and Drug Administration
EFSA European Food Safety Authority
EU European Union
GC Gas Chromatography
GRAS Generally recognised as safe
PAH Polycyclic aromatic hydrocarbon

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