

HEALTH ASPECTS OF NANOCCLAYS USED IN NANOCOMPOSITE FOOD PACKAGING MATERIALS

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Abstract – Clays are naturally found, abundant and nano-sized inorganic materials. Nanoclays are incorporated into packaging films for different purposes such as improving barrier properties, chemical and thermal stability, retardation of flammability and easy recycling as well. Hydrophilic nanoclays are organic modified by treatment with organic compounds such as ammonium ions and surfactants before incorporated in the polymer. Besides these advantages of nanoclays provided in packaging industry, limited numbers of *in vitro* studies have shown potential toxicological effects of nanoclays in humans. Especially modified clays exhibited higher potential toxicity on human cell cultures. In this respect, migration of clay elements into foods has taken into consideration. It has been reported that clay constituents are potential migrants transmitting into food stimulants. Therefore, potential health and safety issues of nanoclays need to be clarified when they are incorporated into nanocomposite packaging materials used in animal or vegetable foods in origin.

Key Words – Migration, Nanoclay, Toxicological effect

I. INTRODUCTION

Packaging is an indispensable application in meat industry to extend the shelf life of meat products. In terms of traditional view, functions of packaging materials involve physical, chemical and biological protection and preservation of the foods [1]. However, recently packaging materials represent much more than shelf life of the foods. Biodegradability, design and health-related concerns are among the other issues related to food packages. Besides common packaging applications such as vacuum packaging and modified atmosphere packaging, novel packaging

technologies have also been introduced to meat industry. While these technologies open new horizons and provide new developments, they have also accompanied some health concerns. This paper looks at new developments related to nanotechnology field in meat packaging industry from the view of consumer health. The purpose of this study is to clarify potential health and safety issues of nanoclays that incorporated into nanocomposite food packaging materials.

II. USE OF NANOCCLAYS IN FOOD PACKAGING

Nanotechnology has provided new approaches to the modern food packaging area by means of clay minerals. Clays are naturally occurring nano-sized inorganic solid materials [2]. The clays most commonly used in the production of nanocomposites are 2:1 layered silicates. Each layered sheet has about 1 nm thickness and length from 10 nm up to microns [3].

Most widely used clay filler is montmorillonite (MMT), which has negatively charged layer surface [4]. Hydrophilic surface characteristic of most clays complicates their homogeneous dispersion in polymer matrix [5]. Therefore, organophilization is necessary by the interaction of layer surface with organic compounds such as ammonium ions. Surfactants are also able to enlarge the space between clay layers to a certain degree. By the organophilization of clays in polymer matrices, intercalated or exfoliated nanocomposites are formed [6]. Figure 1 shows the intercalated and exfoliated nanocomposite forms [7].

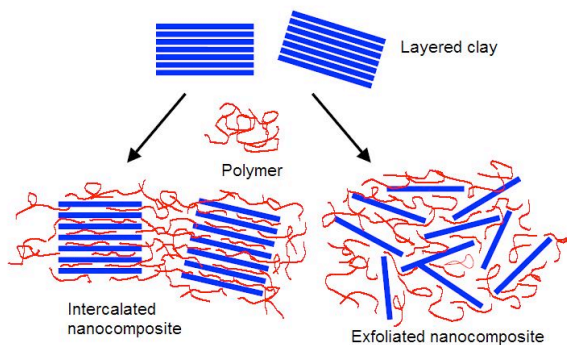


Figure 1. Intercalated and exfoliated nanocomposites from layered clays and polymers

Incorporation of organoclays in polymers provides them numerous benefits including improved barrier properties, chemical and thermal stability, retardation of flammability and easy recycling [8]. In addition to reinforcing packaging materials, nanoclays can provide active properties in the packaging materials, such as antimicrobial and antioxidant activity by means of being carriers of active materials [4]. The metal and metal oxide nanomaterials such as silver, gold, zinc oxide, silica, titania, alumina and iron oxides are commonly used for this purpose [9].

Silver is the most common nanoparticle used in antimicrobial packaging materials due to its strong antimicrobial activity against a wide spectrum of microorganisms [10].

III. HEALTH ASPECTS RELATED TO NANOCLAY TOXICITY

Although numerous benefits of nanotechnology have been introduced, potential hazardous effects of nanoparticles in human health have received little attention. Nano-materials, because of their larger surface areas as compared to those of the materials with same chemical structure, are able to interact with food systems more rapidly when they get in contact with them. On the other hand, nano sized particles can enter our body by the inhalation of contaminated ambient air since they are unable to be caught by the body filter systems [2]. In case of nanoclays, oral pathway is one of the potential routes of exposure to these clays since they are present in food contact materials [11]. In fact, cell walls are the barriers for transition of nanomaterials. However, recent studies have shown that especially hydrophobic nanoparticles

can result in the inclusion into the lipid bilayer of the cell membrane [12].

As other nanomaterials, potential effects of nanoclays in human health are not well-known. There has been no conclusive evidence for negative effects of nanoclays in human health. However, a few *in vitro* studies have been conducted to determine their potential toxicological effects. Toxicity of nanoclays varies depending on various factors such as their hydrophobicity, type and concentration. Unmodified bentonite, which is found abundantly in the earth, and kaolin have been approved in GRAS (generally recognized as safe) status [13]. However, Sharma et al. [14] reported that organo-modified clay resulted in genotoxicity in the *Salmonella*/microsome assay using the tester strains TA98 and TA100 because of the free quaternary ammonium while modified natural bentonite (montmorillonite) did not induce mutations at concentrations up to 141 µg/ml of the crude clay. Maisanaba et al. [11] also found similar results. In another study, both the unmodified nanoclay, Cloisite Na⁺®, and the organically modified nanoclay, Cloisite 93A® significantly decreased the viability of human hepatoma HepG2 cells [15]. Verma et al. [2] investigated the cytotoxic effects of platelet (Bentone MA, ME-100, Cloisite Na⁺, Nanomer PGV, and Delite LVF) and tubular (Halloysite, and Halloysite MP1) type nanoclays on cultured human lung epithelial cells A549 and demonstrated varying degree of dose- and time-dependent cytotoxic effects of both nanoclay types. Moreover, platelet structured nanoclays were more cytotoxic than tubular type. A low but significant level of cytotoxicity was observed at 25 µg/mL of the platelet-type nanoclays while A549 cells exposed to high concentration (250 µg/mL) of tubular structured nanoclays inhibited cell growth.

Kondej & Sosnowski [16] evaluated the influence of bentonite nanoparticles on the surface activity of the pulmonary surfactant which plays an important role in proper functioning of the respiratory system by lowering the surface tension in the alveoli. They found a strong influence of bentonite nanoclay on pulmonary surfactant activity and a change in the dynamic surface properties of the pulmonary surfactant after

contact with the nanoparticles. These results indicated adverse health effects and development of occupational respiratory diseases caused by bentonite contact.

IV. NANOCLAY MIGRATION FROM PACKAGING MATERIALS AND TOXICITY EVALUATION

Migration of hazardous compounds from packaging materials to foods has always been considered as a great problem in the food industry. Migrants such as monomers, oligomers, plasticizers and adhesives from packaging materials frequently migrate from plastic materials and are suspected as potential carcinogenic compounds [1]. Therefore, strict threshold levels have been established for migration of those materials in foods. For example, use of acrylonitrile monomer was banned by Food and Drug Administration (FDA) officials in making plastic bottles for carbonated beverages and beer, and all other acrylonitrile uses were restricted to a maximum permissible migration level of 0.05 ppm [17].

Developments in nanotechnology area continue to emerge, and there is no doubt that its applicability to the food industry will increase. Migration of nanoclays and other nanoparticles into foods is relatively a novel research topic. Therefore, although many government agencies are interested in establishing new regulations about the nanotechnologies, there is still lack of legal regulations in all over the world. Correspondingly, up to date, only a few studies have been reported in the literature to determine the migration of constituents of nanoclays into foods while relatively further reports are available for other nanosized materials such as metal nanoparticles. For example, Echegoyen & Nerin [9] observed the migration of silver nanoparticles from 3 commercially available food containers to food stimulant solutions in different levels. Song et al. [18] also reported silver migration from nanosilver-polyethylene composite packaging materials. In the study of Avella et al. [19], no increase was observed in iron and magnesium contents of vegetables in contact with clay/starch nanocomposite films while they manifested increased levels of silicon. However, the authors

claimed no significant migration of the constituent elements of the clay nanoparticles into the foods. Farhoodi et al. [20] investigated the migration of aluminum and silicon from PET/clay nanocomposite bottles prepared by melt blending PET and Cloisite 20A nanoparticles into an acidic food stimulants stored at 25 °C and 45 °C. Migration process was dependent on the storage time and temperature, and the molar ratio of aluminum and silicon in the acidic was about 23% higher in the samples stored at 45°C.

V. CONCLUSION

Nanoclay minerals are found in the nature abundantly and might be incorporated into the packaging films. Use of nanoclays in the packaging materials has enabled numerous advantages in food packaging systems such as improved barrier properties, chemical and thermal stability, retardation of flammability and easy recycling. However, nanoclays may also contain a risk factor on the human health because of the migration of clay particles into the foods. Studies showed that organic-modified nanoclays may have potential toxic effects on the human cell cultures depending on various factors like clay hydrophobicity, type and concentration. These potential health and safety issues require more attention for the use of nanoclays, and the clay elements migrate into food. In conclusion, further and immediate research is needed to determine potential toxicity of nanoclays used in food packaging materials and to remove the uncertainties about their negative health effects.

ACKNOWLEDGEMENTS

This study was supported by Scientific Research Project Unit of Erciyes University with the code of FDK-2013-4235. We would like to thank to Erciyes University for providing funds for this study.

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