

A Short Review of Light Barrier Materials for Food and Beverage Packaging

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Abstract Photo-oxidation is one of the main causes of food deterioration of great variety of foods, such as dairy products, nuts, meat products, and wine. It causes a loss of both nutritional value and sensorial quality of products and may even leads to the formation of toxic compounds. Active packaging for food and beverages has been investigated and developed with embedding light absorbers or blocking materials into the plastics. In recent years, several novel light barrier materials have been proposed as an alternative option for different applications. This article reviews the up-to-date technology in light absorber and blocking material with special emphasis on chemical compound and mechanism. Inorganic, organic, hybrid organic-inorganic, and natural light absorbers were scoped. The challenges and future perspectives of light barrier materials are also discussed.

Keywords Active packaging, Light absorber, Light sensitive food and beverage, Photo-oxidation

Introduction

Food and beverage have a chance to expose to natural and artificial light during manufacturing, packaging, distribution, storage, display, and consume. The deleterious effects from photosensitized reactions may be resulted in the photo-oxidation or photo-degradation of proteins¹, fat and oil², pigment³, vitamin and chromophore impurities⁴. In the presence of oxygen and light source, the photosensitization generates several reactivated oxygen species (ROS) in form of oxygen radicals (i.e., superoxide anion, hydroxyl, peroxy, alkoxy and hydroperoxy radical) and nonradical derivatives (i.e., hydrogen peroxide, ozone, and singlet oxygen)⁵ causing various undesirable chemical changes in food constituents such as the formation of unpleasant off-flavors, losses of nutritional value, and the discoloration of pigments⁶.

As a novel technology, active packaging is generally designed to incorporate active components into the packaging matrix which is able to absorb or release the compound to the surrounding environment in order to maintain the condition of packaged food or extend the shelf life of the product⁷. Active packaging with light barrier has received special attention due

to the fact that, as one of the most promising alternatives to traditional packaging, light absorber or light blocking agent are included into or coated onto food packaging materials to reduce the photo-oxidation of the food, which is one of the main causes of food degradation. Several studies showed that the rate of photo-oxidation of the food product was mitigated with the lower light transmission of the packaging⁸⁻¹¹.

This review is focused on the light barrier additives used for active packaging. The light sensitive foods and beverages were briefly described to provide the understanding for the reason of product degradation. The recent technique and principal mechanism of light absorbers and the commercialized products were discussed as well. Finally, the challenges and future trends of light barrier packaging were proposed.

Light Sensitive Foods and Beverages

Light sensitive compounds contained in food ingredient are typically called photosensitizers and often refer to pigments such as chlorophyll¹², riboflavin¹³, carotenoids¹⁴, anthocyanin, and flavonoid¹⁵. The photosensitizer molecules generally comprise with chromophore structure that is able to absorb photon energy from light and produce singlet oxygen or ROS. It is reported that a protein and fat rich foods are more susceptible to the light damage via photosensitizer induced photo-oxidation^{16,17}. This is the case with milk and dairy products, meat and meat products, vegetable oils, and wine. Each photosensi-

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Table 1. Examples of light sensitive food and beverage

Food and beverage	Light sensitive nutrients	Wavelength of degradation (nm)	Effects of light on products	Ref.
Milk and dairy products	vitamin A, B ₂ , chlorophylls, unsaturated and saturated fats	326, 415-455, 640-670	loss of vitamins, off-flavor, discoloration	24-28)
Meat and meat products	vitamin B ₂ myoglobin - oxymyoglobin: fresh and frozen meat - nitrosomyoglobin: cooked meat	366, 410-650	discoloration	24, 29, 30)
Vegetable oils	chlorophylls, carotenoids, unsaturated and saturated fats	200-450, 640-670	loss of vitamins, off-flavor, discoloration	31-33)
Wine	vitamin B ₂ , phenolic compounds (anthocyanin)	230-250, 270-350, 440-550	off-flavor, rapid color fading	23, 34)
Dried nuts	unsaturated fatty acids, vitamin B ₂	230-250, 270-350, 440-550	loss of vitamins, off-flavor	35)

Table 2. Chemical reaction of photo-degradation by light and oxygen¹⁹⁾

Initiation (light)	$R-H \rightarrow R\cdot + H\cdot$
Propagation	$R\cdot + O_2 \rightarrow R-O-O\cdot$ $R-O-O\cdot + R-H \rightarrow R-O-OH + R\cdot$ $R-O-OH \rightarrow R-O\cdot + OH\cdot$
Termination	$R\cdot + R\cdot \rightarrow R-R$ $R\cdot + R-O-O\cdot \rightarrow R-O-O-R$ $R-O-O\cdot + R-O-O\cdot \rightarrow R-O-O-R + \text{nonradical products}$

tizer is degraded by absorbing the light of different specific wavelength based on their molecular structure. Table 1 presents a types of food and beverage and the quality affecting by light ranging from UV to visible light.

In the presence of oxygen, the energy of the photons in the light is sufficient to break chemical bonds in photosensitizers, resulting in the formation of free radicals as described in Table 2. In propagation state, the free radicals readily react with other molecules in photosensitizer or polymer chain of protein or unsaturated fat to form oxy and peroxy radicals rendering a chain scission. The reaction continues until two free radicals react with each other followed by forming stable non-radical compounds in termination state^{18,19)}. The photosensitizer induced photo-oxidation is able to change the chemical structure of protein in milk and dairy product, causing different types of chemical modifications including fragmentation of covalent bonds, generation of carbonyl compound, cross-linkages, and various changes in a wide range of different amino acids²⁰⁾. On the other hand, the excited free radicals from initiation state promptly react with fatty acids in the meat and meat product, resulting off-flavor^{21,22)}. In addition, the quality of wine can be dropped with a decrease of monomeric anthocyanin content and an increase of polymeric pigments by photochemical degradation reactions²³⁾.

Current Technology of Light Absorber

Recently, light-barrier active packaging has been more

interested in food industry replacing the traditional approach by direct addition of the antioxidant agent into the food. Aluminum/metallize foil is considered as the best material for UV and visible light blocking. However, it poses some drawbacks regarding recyclability, high cost, and non-transparency. Currently, the use of UV absorbers takes advantage over such demerits³⁶⁾ with smart selection and application to the appropriate polymer since each of them are designed and developed for specific function.

1. Inorganic Light Absorbers

Inorganic materials are based mainly on the metal oxide particles that are able to absorb or scatter the light. Many inorganic UV absorbing systems have been developed such as titanium dioxide (TiO₂), cerium oxide (CeO₂), iron oxide (Fe₂O₃), zirconium dioxide (ZrO₂), and zinc oxide (ZnO)³⁷⁾. The attenuation of the light in these materials is accomplished by "pigment theory" via two pathways; bandgap absorption and light scattering¹⁹⁾. Theoretically, any semi-conductive metal oxide particles are capable of absorbing the photons of light energy depending on their band gap energy. The light absorption will occur when the photon energy is equal or greater than the band gap³⁸⁾. CeO₂, TiO₂, and ZnO have a similar band gap energy at about 3.2 eV which can absorb only UV light ($\lambda < 380 \text{ nm}$)³⁹⁾. Several researches attempted to reduce their band gap by doping with transition metals to make it able to absorb the visible light ($\lambda > 380 \text{ nm}$) or solar light^{40,41)}.

Apart from the band gap property, the high refractive index

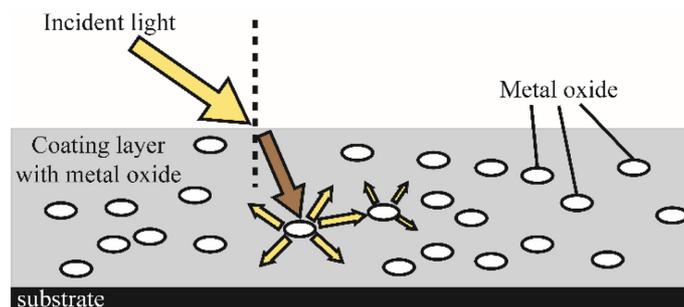


Fig. 1. Schematic representation of light absorption and scattering of metal oxide⁴⁵).

of metal oxide particles also plays as a crucial role for light blocking by light scattering. The ability of metal oxide particles to reflect, refract, and scatter light is due to its internal crystal structure. Generally, the refractive indexes (n) of conventional polymers are limited to 1.6⁴²). The incorporation of high refractive index inorganic compounds, such as TiO_2 ($n \sim 2.5$ and 2.7, in the crystal forms of anatase and rutile, respectively)⁴²) and ZnO ($n \sim 2.0$)⁴³), into polymer can synergistically increase the refractive index of polymer matrix resulting the higher light scattering and blocking performance. Fig. 1 displays a simple scheme of light scattering and absorption behavior. The power of light scattering is influenced by the several factors such as incident light wavelength, shape and size of particle, and media. The scattering intensity is generally not strongly dependent on the wavelength, but is quite sensitive to the particle size⁴⁴).

Study from Hashimoto and Sakamoto⁴⁶) showed that an oriented polypropylene film coated with peroxy-modified anatase TiO_2 blocked 99.2% of the short-wavelength UV light (200-300 nm) and 70.9% of the long-wavelength UV light (300-400 nm). Ren et al.⁴⁷) enhanced the UV shielding performance of polyvinyl alcohol by using 2 wt% rutile TiO_2 . The composite film exhibited the great light barrier with <10% light transmittance over 200-800 nm range. Typically, the rutile TiO_2 showed a lower UV transmittance than anatase TiO_2 because of the higher scattering effect of rutile TiO_2 ⁴⁸). Lizundia et al.⁴⁹) developed an efficient UV-shielding coatings for packaging applications by applying ZnO nanoparticle to poly(l-lactide). With the addition of 5 wt% ZnO , the nanocomposite film was able to reduce nearly 80% of UV light transmittance, while activity in the visible region was negligible.

2. Organic Light Absorbers

One of the most important UV-absorbers is organic compounds. In general, they are developed to be colorless or nearly colorless (light yellowish) with high absorption coefficient in the UV range. Phenolic-type UV absorbers take a larger share in the market of organic UV absorbers because they are able to absorb the light energy and transform into less harmful

energy. Moreover, they exhibit good photo-stability. In chemical structure, the phenolic-type UV absorbers are typically involved with hydrogen bond from either O–H–O bridges (e.g., hydroxyl benzophenones or hydroxyl flavones) or O–H–N bridges (e.g., xanthenes, salicylates, hydroxyphenyl benzotriazoles, and hydroxyphenyl triazines). The intramolecular hydrogen bonds possess efficient dissipation energy in changing the incident light energy to low thermal energy by means of photo-physical reactions and thereby retard the formation of free radicals in the early stage of degradation^{19,37}). Another group of the organic UV absorber is non-phenolic type such as oxanilides and cyanoacrylates. The presence of intramolecular H-bonds between carbonyl and imine groups and a trans-planar geometry are believed to be a main functional group for quenching the transmitted light. Table 3 presents various types of UV absorbers available in the current market. Several researches had evaluated the light absorption efficiency of the commercial organic UV absorbers with the real packaging and food^{8,23,50}). Coltro et al.⁸) reported that the use of a small concentration (0.080 wt%) of Tinuvin® 326 promoted the light barrier of PET bottle with 90% reduction of the light transmission at 360nm wavelength.

3. Hybrid Organic-Inorganic Light Absorbers

A hybrid material is defined as a material that comprised of different moieties blended on the molecular scale resulting the remarkable superior properties to those of their components⁵¹). Hybrid UV absorbers can refer to the two combination systems; (1) combination with organic UV absorbers and inorganic porous matrices and (2) integration of inorganic UV absorbers with organic polymers.

As shown in Fig. 2, the hybrid material can be obtained either by the synthesis of inorganic UV absorber within the organic polymer matrix or the polymerization of an organic monomer covering the inorganic phase of UV absorber. The phenolic-type UV absorbers (2,2'-dihydroxy-4-methoxybenzophenone) are blended with silicon alkoxides via simple sol-gel technique. With the method involved the hydrolysis and condensation of silicon alkoxides, modified alkoxides with

Table 3. Organic UV absorbers currently applied in food packaging

	Trademark	Chemical class	Absorbed wavelength (nm)	Applied polymer						
				PO	PVC	PS	PEST	PA	PC	PMMA
Organic Absorbers	Tinuvin® P	Hydroxyphenyl benzotriazole	300-400		•	•	•		•	•
	Tinuvin® 326	Hydroxyphenyl benzotriazole	300-400	•			•			
	Tinuvin® 1577	Hydroxyphenyl triazine	250-360				•	•	•	
	Uvinul® 3034	Benzotriazole	240, 280-360	•			•	•	•	•
	Uvinul® 3030	Cyanoacrylate	240-320				•		•	
	Uvinul® 3035	Cyanoacrylate	240-320		•		•	•		
	Chimassorb® 2020	HALS	200-250	•	•					
	Chimassorb® 81	Benzophenone + HALS	280-350	•	•					

HALS: hindered amine light stabilizers, PO: polyolefin, PVC: polyvinyl chloride, PS: polystyrene, PEST: polyester, PA: polyamide, PC: polycarbonate, PMMA: polymethylmethacrylate

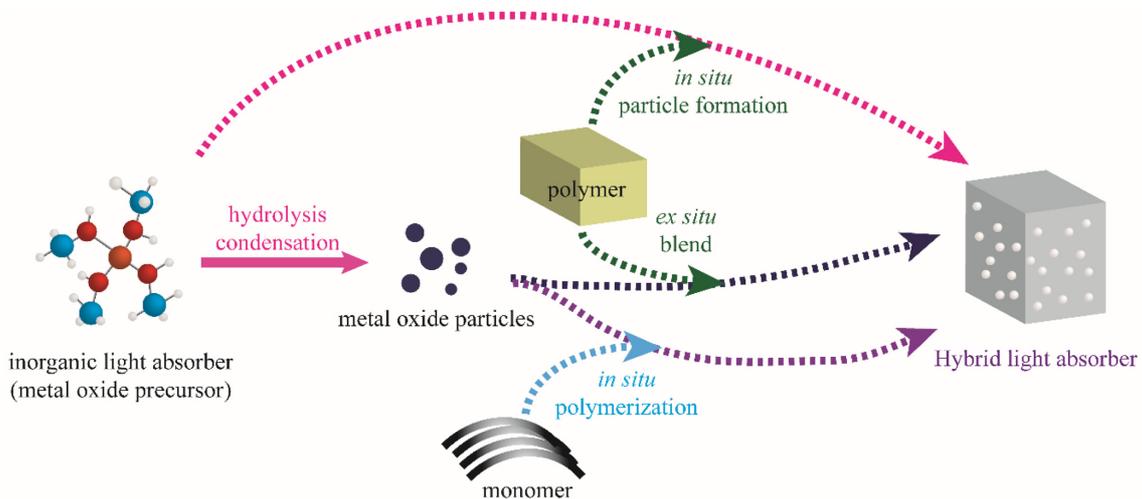


Fig. 2. Different synthetic pathways for hybrid organic-inorganic light absorber via the *in situ* and *ex situ* methods. (Reprinted from [37], copyright 2012, with permission from the John Wiley & Sons, Inc.)

non-hydrolysable phenyl groups are obtained as a template for deposit the organic UV absorber molecules. The advantage of using modified alkoxides is to entrap greater amount of the organic UV absorber molecules resulting in stronger absorption in the UV range^{19,52}. The synergic effect can also be expected when integrating the organic polymer whose optical absorption is active in $\lambda < 300$ nm with the amorphous TiO₂ or crystalline anatase TiO₂. Cao *et al.*⁵³ developed a strong hybrid UV-shielding material by dispersing the intercalated layered double hydroxides (LDHs) into poly(ethylene terephthalate) (PET) via a facile solution mixing procedure. The micro- and nanoparticle of inorganic LDHs improved the light blocking performance of PET by lowering 30.7% and 46.8% of the average light transmittances, respectively. Li *et al.*⁵⁴ proposed a new technique for the synthesis of the transparent high UV shielding poly(methyl methacrylate)-ZnO nanohy-

brid materials through *in situ* free-radical sol-gel polymerization. With the 0.017 wt% loading of ZnO quantum dots, the light transmission of the obtained nanohybrid material in the UVB range up to 340 nm was approximately reduced to zero, while the transmission value in the UVA and visible light was increased. Zhang and Han⁵⁵ prepared a hybrid microcapsule from TiO₂ and ZnO with poly(vinyl acetate) by *in situ* emulsion polymerization. The poly(lactic acid) film embedding the as-prepared microcapsules exhibited strong light barrier due to the intrinsically UV shield of matrix resin and metal oxide particles.

4. Natural Light Absorbers

Natural UV absorbers are widely interested for academia and industrial community because it can reduce several risks from food contamination by migration of the synthetic UV

Table 4. Various natural light absorbers and their performance

UV Absorber	Content (%)	Polymer matrix	Color of the obtained polymer	Light blocking performance (% decrease of light transmittance)				Ref.
				UVC	UVB	UVA	Visible Light	
Sepia eumelanin	0.5 wt%	poly(vinyl alcohol)	Yellow to light brown	100%	>98.5%	30%	-	58)
Rosin	20 wt%	Poly(lactic acid)	White with transparence	100%	98%	92%	53%	22)
Betel extract	30 wt%	Sago starch	Light green	-	-	>98%	-	59)
Cassava fibrous	3 wt%	Cassava starch	White with opacity	40%	35%	35%	10%	60)
Tea catechins	1.65 wt%	Methylcellulose	Light orange	100%	>98.5%	>90%	20%	61)

absorbers. Several researchers tried to employ the light barrier property of natural materials into food packaging as presented in Table 4. The research revealed that the natural light absorbers have a good performance in the wide range of light wavelength. This could be from the phenolic compounds or chromophore in their chemical structure^{56,57}. Wang et al.⁵⁸ proposed to use sepia eumelanin nanoparticles, a biomacromolecule isolated from the inks sacs of cuttlefish, as UV-absorber for poly(vinyl alcohol). The obtained transparent film was able to block nearly 100% of UVC, over 98.5% of UVB, and 30% of UVA. Narayanan et al.²² improved the light barrier of poly(lactic acid) by fabricating with a rosin. The composite film demonstrated noteworthy light barrier feature by shielding the passage of 98% of UVB, 92% of UVA, and 53% of visible light regime.

Challenges and Research Perspectives

The light absorber materials have been widely used in food packaging, in particular, for light sensitive foods and beverages. Various researches have been conducted to evaluate the performance of the commercial light absorbers as well as to develop the new material with higher performance. With the combination of light absorption and scattering, the inorganic compounds show a good performance of light blocking in broad spectrum of UV light (UVA and UVB) coverage. However, the scattering extends into the wavelengths of visible light and produces the effect of whiteness and opaque to the human eye. This appearance possesses an obstacle in the marketing point of view. Several studies reported the migration of organic light absorber into food and food simulants⁶²⁻⁶⁴ warning a precaution to manufacturer when applying into their product. Hybrid organic-inorganic light absorbers are considered as a promising approach. It can provide a superior light barrier property over the wide range of light wavelength due to the synergic effect of polymer matrix and light absorber. However, this technique is limited by the polymer type and synthesis technique. Moreover, the agglomeration of metal oxide during polymerization can drop the light scattering performance. In addition, most of natural light absorbers are derived

from pigments or photosensitizer which provide a vivid color to polymer matrix and required to avoid light exposure.

To provide an appropriate light absorber to packaging manufacturer and to encourage the consumer to accept these technologies, the aforementioned drawbacks of each material have to be solved. The advanced polymerization technique and nanotechnology have been considered as an excellent approach for developing or improving the performance of light barrier material. Zhang and Han⁵⁵ reported that during polymerization, the dispersion of inorganic light absorber in polymer can be promoted by organic coating on metal oxide particles. It was reported that coating the surface of TiO₂ with either polyhedral oligomeric silsesquioxanes⁶⁵ or poly(ϵ -caprolactone)⁵⁵. Moreover, several novel polymerization methods, such as mini-emulsion-combined sol-gel polymerization,⁶⁶ vapor deposition polymerization,⁶⁷ and atom transfer radical polymerization⁶⁸, have been proposed in order to acquire the higher barrier performance.

Conclusion

The light from nature and artificial light sources, especially UV, is one of significant factors for quality deterioration of food and beverage. In this review, the diverse types of light absorber for protection the quality of food and beverage from the light were briefly discussed. The four classes of chemicals, inorganic, organic, organic-inorganic hybrid and natural compounds were introduced and demonstrated regarding their properties and active mechanisms. Although the inorganic and organic UV absorbers have a high efficacy for light absorption, safety, recyclability and aesthetic issues are still existed in a marketing standpoint. The use of hybrid material is promising with greater performance but only literature reports are currently available. In accordance with the global trends of sustainability and eco-friendly material, many researchers participate in the development of natural UV absorbers; however, the photo-stability problem has to soon be addressed. With the harmonization of emerging nanotechnology and advanced fabrication process, it is highly expected that an innovative light barrier packaging will be advent in near future.

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