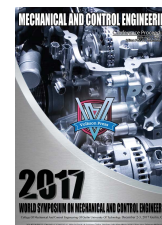




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## CHARACTERIZATION OF THE UV - VISIBLE ABSORPTION SPECTRA OF COMMONLY USED PHOTOINITIATORS

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### ARTICLE DETAILS

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### ABSTRACT

UV-LED curing has the advantages of energy saving and no ozone, mercury pollution has become one of the recently developed green printing technology. The photoinitiator used to meet the requirements of food packaging materials, but also in the LED issued by the central wavelength of 385nm or 395nm light absorption can stimulate the photopolymerization. In this paper, the absorption spectra of 12 kinds of photoinitiators, such as TPO, BDK, ITX, DETX, 819, 784, TPO-L, 127, 369, MBF, 199, 796, were characterized by UV-Vis spectrophotometer. Prepared UV-LED curing varnish, The performance of the photoinitiator was analyzed. According to the requirements of food safety regulations, the photoinitiators which could be used for UV-LED curing were obtained TPO, TPO-L and 819.

## 1. Introduction

Photoinitiators, also known as photosensitizers or photocuring agents, are substances that absorb radiant energy and undergo chemical changes to produce reactive intermediates that initiate polymerization. Can lead to monomer, oligomer and polymer unsaturated double bond crosslinking curing [1]. The photoinitiator (PI) absorbs the energy under the ultraviolet light and undergoes an electronic transition, which changes from the ground state to the excited state (PI\*) and then decomposes into free radicals; Radicals react with the other components (M) of the photoluminescent groups that contain photocurable groups and continue to polymerize to form chain-like growth, accompanied by the transfer and termination of free radicals in the growing chain [2]. Photoinitiation systems are either one-component (photoinitiator) or some two-component or multi-component (photoinitiator/ additive). Photoinitiator is the key factor to control the photopolymerization process. The efficiency of photoinitiator is directly determined by its light absorption (absorption wavelength, molar extinction coefficient) and reactivity [3].

UV-LED curing was developed on the basis of UV curing · It is a technology that can be rapidly cured under the LED central wavelength of 385nm or 395nm, which has the advantages of energy saving, ozone-free and mercury pollution [4]. UV-LED curing varnish or ink is coated, printed, LED radiation curing into a film, in which some of the remaining photoinitiators may be through chemical migration or physical contact migration from the food package to the food inside the package, Thus polluting the products in the package, causing potential harm to human health. November 23, 2015 Switzerland Introduces Two Catalog Lists of Regulations Concerning Food Packaging Materials (RS 817.023.21) · List A refers to materials that are suggested for using in food packaging, and List B refers to some materials that can be used but have not yet been fully validated. At present, Europe and the United States refer to the contents of the Swiss regulations and Nestle's norms for the material requirements of food printing. Both of these requirements need to be met at the same time [5]. China Tobacco Corporation industry standard YQ69-2015 "cigarette and box packaging paper safety and health requirements" clearly defines the limit of the photo-initiator residue after printing and banned photoinitiator catalog. These regulations make it clear that photoinitiators in materials used in food packaging materials must meet the requirements [6]. In this

paper, the commonly used initiator in food packaging materials for absorption spectroscopy test, expecting to obtain a photoinitiator which meets the requirements of food packaging materials and which can be excited under the illumination of LED.

## 2. EXPERIMENTS

### 2.1 Experimental photoinitiators

The photoinitiator used in this experiment was purchased from Shanghai Guangyi Chemical Co., Ltd., Guangzhou Lihou Trading Co., Ltd. and Tianjin Jiuri Chemical Co., Ltd. The following Table 1 shows the various properties of the photoinitiators.

**Table 1:** Different properties of different photoinitiators

product name	Chemical type	Exterior	CAS No.	Molecular weight	Melting point (in methanol solution)	Absorption wavelength
Irgacure 127	$\alpha$ -hydroxy ketones	White powder	474510-57-1	340.4	82-90°C	259nm
Irgacure TPO	Monoacylphosphine	Light yellow powder	75980-60-8	418.5	88-92°C	295nm, 368nm, 380nm, 393nm
Irgacure 819	Diacyl phosphine	Light yellow powder	162881-26-7	418.5	127-133°C	295nm, 370nm
Irgacure 369	$\alpha$ -hydroxy ketones	Light yellow powder	119313-12-1	366.5	110-114°C	233nm, 324nm
Irgacure MBF	Phenyl ethanediamide	Transparent yellowish liquid	15206-55-0	164.2	17°C	255nm, 300nm
Irgacure 784	Metallic compounds	Orange powder	125051-32-3	534.4	160-170°C	520nm
Easepi 199	Benzophenone derivatives	White powder	Patent Protection	A small molecule type	82-84°C	220nm, 280nm photoinitiator
Photoinitiator BDK	Benzoin dimethyl ether	White crystalline solid	[24650-42-8]	256.3	64-66°C	220nm, 255nm, 325nm
Photoinitiator ITX	2-isopropylthioxanthone	Light yellow crystal	5495-84-1	254.3468	74-76°C	250nm-390nm

Photoinitiator DETX	2,4-diethyl thioxanthone	Yellow powdery solid	82799- 44-8	268.37	70-75°C 261nm,385nm
Photoinitiator TPO-L	Ethyl 2,4,6- trimethylbenzoylphenylphosphonate	Yellow transparent liquid	84434- 11-7	316.33	299nm, 366nm
Photoinitiator 796		Light yellow Patent powder Protection			260nm,335nm

### 3. UV - visible light absorption spectroscopy test

The experimental instrument is UV - visible spectrophotometer, model UV-2501PC, The photoinitiator solution was prepared by dissolving various photoinitiators selected in the acetonitrile solvent at a mass fraction of 0.01% at room temperature. Respectively, take appropriate photoinitiator solution and acetonitrile solvent in a quartz cuvette, In contrast to the acetonitrile solution, the UV-vis spectrophotometer was used for testing to determine the UV absorption spectra of different photoinitiators. For the photoinitiators which may be used for UV-LED curing, the varnish was prepared and the light stability and curing property of the varnish were analyzed.

### 4. RESULTS AND DISCUSSIONS

Figure 1 and Figure 2 show the UV absorption spectra of photoinitiators TPO and TPO-L, respectively.

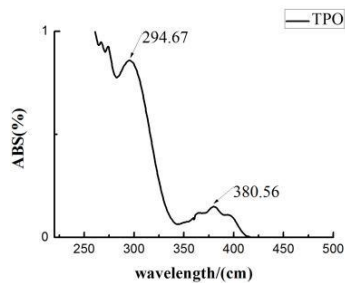


Figure 1: Ultraviolet Absorption Spectra of Photoinitiator TPO

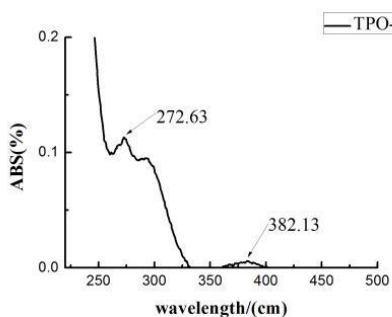


Figure 2: Ultraviolet Absorption Spectra of Photoinitiator TPO - L

It can be seen from Figure 1 and Figure 2 that the absorption peak of photoinitiator TPO is about 290 nm and about 380 nm, while the absorption peak of photoinitiator TPO-L is about 272 nm, Comparing the two curves, it can be seen that the absorption intensity of TPO is greater than the absorption intensity of TPO-L. Because TPO-L is a liquid that contains less components than TPO, the absorption is lower than that of TPO.

Figure 3-Figure 12 show UV absorbance spectra of photoinitiators 127, MBF, 819, 199, 369, 784, 796, BDK, DETX and ITX, respectively.

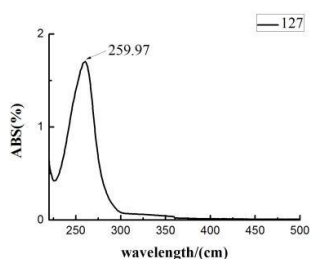


Figure 3: Ultraviolet Absorption Spectra of Photoinitiator 127

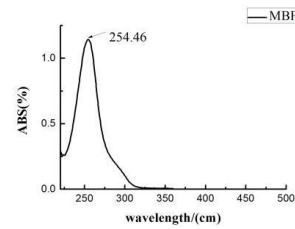


Figure 4: Ultraviolet Absorption Spectra of Photoinitiator MBF

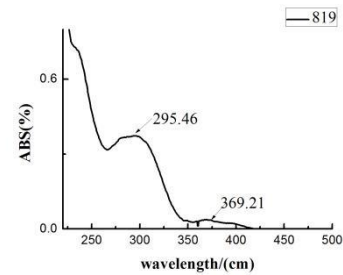


Figure 5: Ultraviolet Absorption Spectra of Photoinitiator 819

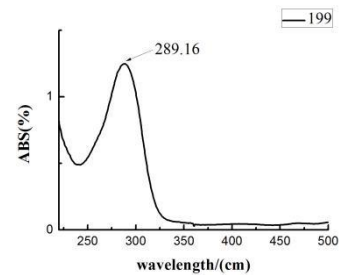


Figure 6: Ultraviolet Absorption Spectra of Photoinitiator 199

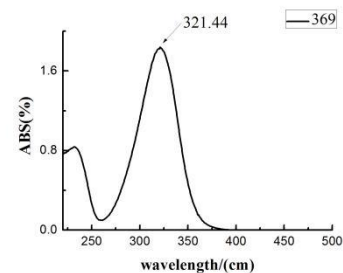


Figure 7: Ultraviolet Absorption Spectra of Photoinitiator 369

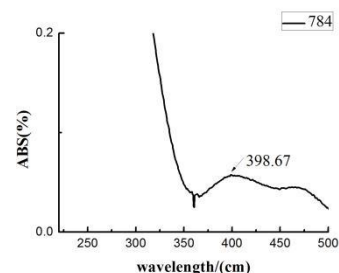
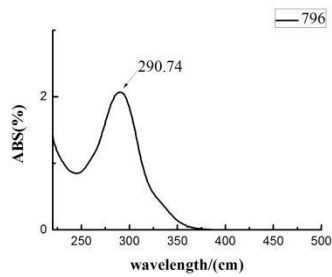
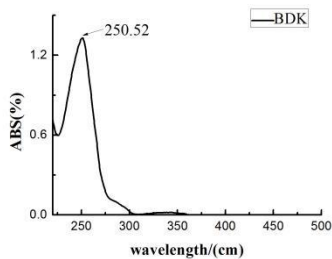


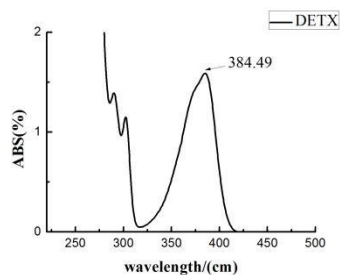
Figure 8: Ultraviolet Absorption Spectra of Photoinitiator 784



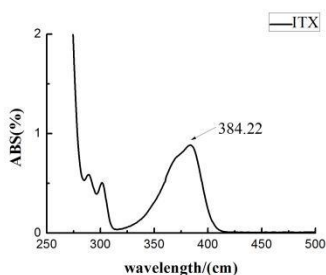
**Figure 9:** Ultraviolet Absorption Spectra of Photoinitiator 796



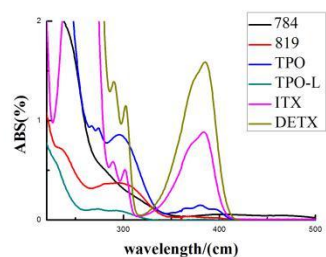
**Figure 10:** Ultraviolet Absorption Spectra of Photoinitiator BDK



**Figure 11:** Ultraviolet Absorption Spectra of Photoinitiator DETX



**Figure 12:** Ultraviolet Absorption Spectra of Photoinitiator ITX



**Figure 13:** Ultraviolet Absorption Spectra of Six Photoinitiators

It can be seen from Figure 13 that there are 819, TPO, TPO-L, ITX, 784 and DETX with wavelengths between 360 and 400 nm. Among them, 784 absorption wavelength of 398.67nm, 819 absorption wavelength of 295.46nm, 369.21nm, TPO absorption wavelength of 294.67nm, 380.56nm, TPO-L absorption wavelength of 272.63nm, 382.13nm, ITX absorption wavelength of 384.22nm, DETX absorption wavelength of 384.49nm. 784 itself is orange in color and is very unstable. The formulated varnish stabilizes for about half an hour under indoor lighting in white light, so the 784 is not suitable for UV-LED curable printing inks or varnishes. ITX will migrate, contaminate the food in packaging. In 2005, Nestlé milk powder recalled 2 million liters of milk powder in the European market because of product packaging exuding ink (ITX), and one year after another found some residuals in the drinks, but it was restricted in YQ69-2015. Therefore, the photoinitiator ITX can not be used a large number of in UV-LED curing varnish. DETX is forbidden to use in YQ69-2015, it can only be used in non-food packaging printing materials. TPO, TPO-L, 819 is a phosphine oxide photoinitiator with long absorption wavelength, good storage stability and little yellowing, so it is suitable for UV-LED curing varnish or ink.

## 5. CONCLUSIONS

Photoinitiators are a key component of UV-LED curing materials and play a decisive role in the cure rate of photo-curable materials. The development direction of photoinitiators are photoinitiators with high absorption intensity, large activity, shallow color, not yellowing, good solubility and low toxicity near 385nm or 395nm wavelength. The selected photoinitiators should be non-toxic to the human body, in line with the requirements of normative international legal documents on food safety. UV spectrum of the 12 common kinds of photoinitiators tested and analyzed showed that: Photoinitiators TPO, TPO-L, 819 can be used in UV-LED curing varnish or ink and other light-curing materials.

## ACKNOWLEDGMENTS

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