

The effectively utilization of oxygen in the process of photopolymerization

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Abstract: Oxygen has long been considered to be unfavorable to UV-curing, for its inhibition effect on the free radical polymerization. However, the inhibition effect of oxygen can be take full advantage in many ways. In this paper, several benefits of oxygen are discussed in detail. First, oxygen can be a protective substance in the process of transportation and synthesis of monomers and/or oligomers. Second, in multi-layer thick coatings, the very top lay of the surface can not be completed curing for the oxygen inhibition, which will be conducive to better bonding of layer by layer. Third, microsphere products which completely polymerized inside and incompletely on surface, so-called gradient material can be obtained when the oxygen was introduced into the photopolymerization system before light irradiation. The active group remained on the surface could further react with other active substances to prepare organic - organic hybrid composites. Another important role of oxygen inhibition is to make the application of light-curing adhesive in the non-transparent material be achieved.

Keywords: oxygen inhibition, UV-curing, gradient material, light-curing adhesive.

Introduction

Radiation curing has experienced a steady growth for the past decades because of its distinct advantages, namely, solvent-free formulations cured upon illumination at the mild environment and temperature conditions. This technology is now commonly used in various industrial fields such as protective coatings, printing inks, adhesives,

varnishes and composites. Most UV-curable resins are based on multifunctional acrylate monomers and oligomers which generate highly cross-linked polymers by a photoinitiated free radical polymerization^[1]. As the UV-curing coating is usually carried out in the air, the presence of oxygen has been a great influence on the cured films. The free radicals formed by the photolysis of the initiator are rapidly scavenged by O₂ molecules to yield peroxy radicals. These species are not reactive towards the acrylate double bonds and can therefore not initiate or participate in any polymerization reaction.

In order to overcome the effect of oxygen inhibition, a lot of research and a number of solutions have been done, such as addition of amine to consume the O₂, increasing the intensity of radiation to accelerate the curing rate and reduce the contact time with oxygen, the most efficient way is filled with inert gas (N₂ or CO₂) to separate the coating and the oxygen, and K. Studer et al.^[2] have found that the effect of CO₂ is better than the O₂.

Although the oxygen inhibition was adverse on polymerization, we found that the oxygen inhibition effect can also be used effectively in practice. (1) The presence of oxygen can prevent monomers or oligomers to deterioration in the process of transport and storage, even in the process of synthesis and preparation of monomers or oligomers. (2) In multi-layer thick coatings, the very top of the surface is not completely cured for the oxygen inhibition, which will be conducive to better bonding of layer by layer^[3]. (3) To make the application of UV-curing adhesive in the non-transparent material be achieved. (4) Microsphere products which highly crosslinked inside and looser crosslinked on surface, so-called gradient material^[4], can be obtained when the oxygen was introduced into the photopolymerization system before light irradiation.

In this paper the effectively utilization of oxygen in polymerization are discussed in detail, especially in the preparation of the polymer materials with special structure. The polymer microspheres prepared by such UV-curing technology was with a cross-linking degree adjustable, cross-linking density gradient rendering features, due to the various conditions during the reaction stages. The product of such a structure

could be further processed and modified, and be applied to the printing plate, three-dimensional model of the production, printing ink, coatings, adhesives, food packaging and biomedical materials field.

Experimental

1. The formulas of UV-curing adhesive used in non-transparent material is composed by the epoxy acrylate oligomer CNUVE151 (20%, Sartomer) and 828 (30wt%, Sanmu, Jiangsu), monomer 1,4-butanediol diglycidyl ether (50wt%, Changxing, China) and **photoinitiator 6976** (3wt%, Huatai, Jiangsu). The formula was coated on the tinplate by 10mm×20mm and exposed to curing in UV Curing machine (RW-UVAC301-40bh, RunWing Co., China). The samples were made as follow (Figure1.). The adhesive strength can be expressed by the maximum tensile load which was measured by Universal Mechanical Tensile Machine (3365, Instron, USA).

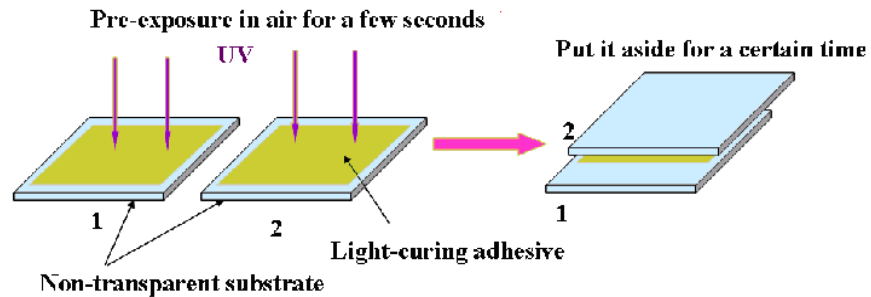


Figure 1. Schematic diagram of sample preparation

2. The materials for preparation of gradient microspheres are: methyl methacrylate monomer (Beijing Chemical Reagent Company), cross-linking agent TPGDA (Sartomer) and photoinitiator Irgacure 1173 (Ciba). The photopolymerization was conducted in UV Curing machine ([RW-UVAP32-36](#), RunWing Co., China). The operation diagram was showing as follow (Figure2).

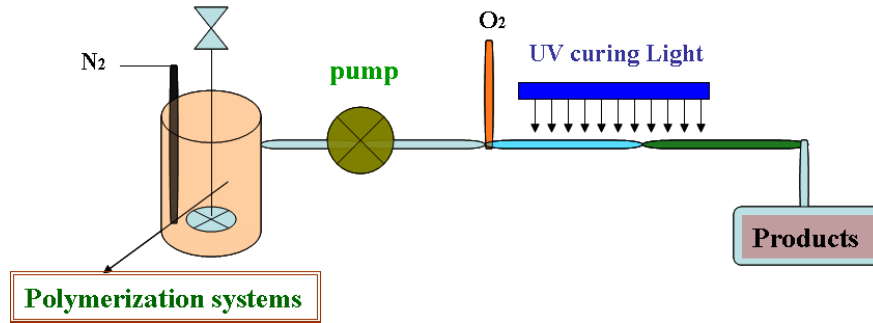


Figure 2. Operation diagram of continuous photopolymerization

The density of microspheres was measured by the pycnometer method, and the micro-topography was measured by scanning electron microscope (Model S-450, Hitachi, Japan). The T_g was measured by DSC analyzer (204 F1, Netzsch, Germany).

Results and discussion

1. The wide application of UV-curing adhesive on the transparent material is because of the fast curing reaction speed. However, non-transparent materials can not be applied because light can not be passed through. Utilizing of oxygen inhibition make the UV curing adhesive of non-transparent materials possible. The appropriate adhesive was coated on one side of the non-transparent substrates, and pre-exposure to UV source for a period of time, due to oxygen inhibition, the surface of coatings will not be cured completely, when the two substrates were bonded closely together, and put them aside for a period of time, the reaction will continue, two substrates will be stick together tightly. The time for complete curing and the bond strength between the substrates are related with the formula and the pre-exposure time.

Table 1. Maximum tensile load (N) with different pre-exposure and

laying-aside time

Conditions	Laying aside for 1 h	Laying aside for 5 h	Laying aside for more than 12 h
Pre-exposed for 1min	Cured uncompletely	148 N	1354 N
Pre-exposed for 2min	109 N	171 N	1343 N

From the table above it can be seen that when the pre-exposure time is shorter, more time is needed in order to continue to cure, when the cured finished, the maximum tensile load are the same.

2. For the formation of microspheres (table 2), there are many factors that must be considered, monomer concentration, initiator ratio, cross-linker ratio, solvent type and ratio. Every one of the factors will impact on the micro-sphere structure.

Table 2. Composition of cross-linking PMMA particles

NO.	MMA (g)	1173 (g)	TPGDA (g)	Water (ml)	Ethanol (ml)	Irradiation time (min)
TP1	20	0.10	0.2	100	100	30
TP3	20	0.10	0.6	100	100	30
TP5	20	0.10	1.0	100	100	30
TP7	20	0.10	1.4	100	100	30
TP10	20	0.10	2.0	100	100	30

Scanning electron microscopy (SEM) of the particles

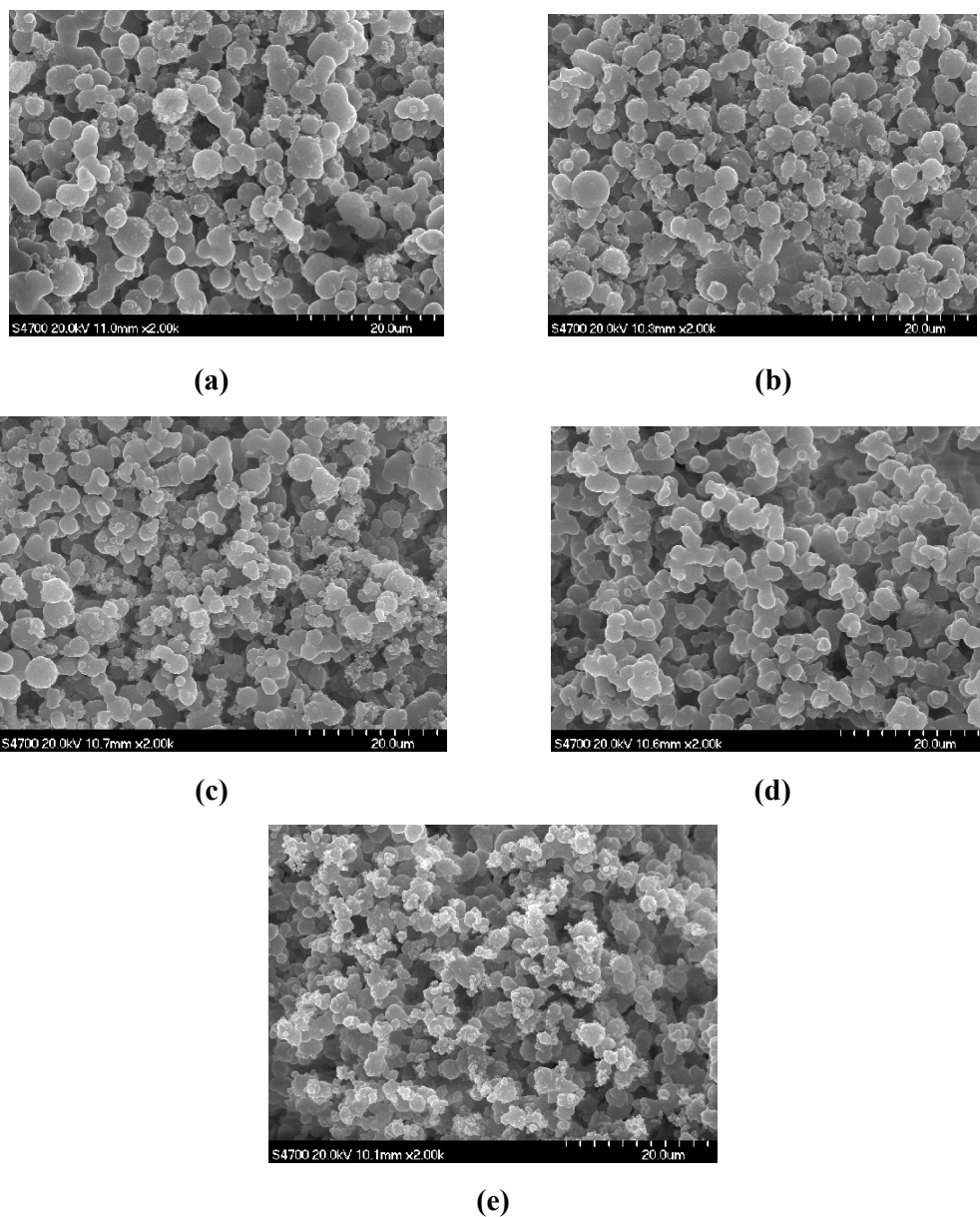


Figure 3. SEM of PMMA particles (a)TP1;
(b)TP3;(c)TP5;(d)TP7;(e)TP10

As can be seen from the figure above, the particle size decreased with the increase of crosslinker content, and TP10 has the smallest particle size. The dry particle size was range from 1µm to 4µm.

In the polymerization process of TP1, TP3, TP5, TP7, and TP10 particles, the reaction conditions are the same, so the solubility and the precipitation critical chain length of the polymer product were also the same. But with increase of the

cross-linker ratio, the molecular chain and degree of cross-linked polymer particles increased at the same time, so the product precipitate out from the solvent with smaller particles.

The density of PMMA particles

Table 3. The density of obtained particles

NO.	Density (g/cm ³)
TP1	1.058
TP3	0.999
TP5	0.995
TP7	0.851
TP10	0.954

As showing in the table 3, the density of particles of TP series decrease as the cross-linking agent content increase. On the one hand, micro-gel formed in the initial stage of polymerization and some of the monomer was pre-embedded into the micro-gel. The more monomer was pre-embedded into the micro-gel, the grater relative mass loss of the network structure, resulting in a decline in particle density. On the other hand, the higher degree of cross-linking, the more network structure formed in the particles, which also conducted a decrease of the density.

The DSC results of PMMA particles

Table 4. The glass transition temperature (T_g) of PMMA particles

NO.	T _g (□)
TP1	127.5
TP3	123.3
TP5	122.8
TP7	100.1
TP10	108.7

It can be seen from Table 4, as the cross-linking agent content increases, the glass transition temperature decreased gradually.

The factors that affect the T_g of materials are: cross-linking density and the residual monomer content. On the one hand, with the increase of cross-linking agent content, the cross-linking density and the T_g value should be a corresponding increase, but the copolymer will cause the T_g value decreased, so there was a competition impact of copolymer and cross-linking density on the T_g. On the other hand, the residual double bond content of the material will also affect the T_g value, the higher residual double bond content, the lower value of T_g. The infrared spectra of all particles have absorption peaks in 1640cm⁻¹, which represent the stretching vibration of carbon-carbon double bond. This result indicated that there were residual carbon-carbon double bond exist in the particles (as showing in Figure 4). As can be seen from Table 5, the order of the residual double bond content was: TP7> TP5> TP3> TP1, and the order of the T_g was the same. Thus proved that the residual double bond content was a great influence on the T_g of the material.

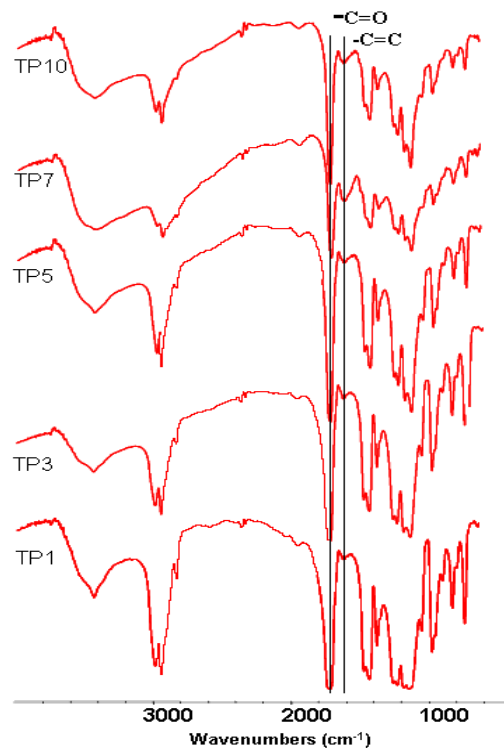


Figure 4. IR spectra of PMMA particles

Table 5. The C=O and C=C peak area and proportion obtained from IR spectra

NO.	-C=O peak area	-C=C peak area	-C=C peak area /-C=O peak area
TP1	7498.96	168.97	0.0225
TP3	132.333	4.566	0.0345
TP5	102.801	6.814	0.0663
TP7	17.676	6.788	0.3840
TP10	58.915	6.761	0.1148

Conclusion

Studies have shown that light-curing of the adhesive in the application of non-transparent materials can be achieved. The adhesive effect was related with the

concrete formulations and curing condition, as well as other factors, which need further study.

The PMMA particles with gradient of cross-linking of the network structure can be prepared via UV light by regulating the content of cross-linker, and combined with the role of oxygen during polymerization. There are residual unreacted double bond on the surface of these networks, which contribute to the further reaction of the substrate with other resins to improve bonding with the resin matrix.

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