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# Effect of cuprous oxide with different sizes on thermal and combustion behaviors of unsaturated polyester resin

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## HIGHLIGHTS

- $Cu_2O$ particles were prepared with average particle-size of 10, 100, and 200 nm.
- Different-sized $Cu_2O$ influenced the combustion behaviors of UPR observably.
- $Cu_2O$-S promoted completely combustion of UPR and reduced the gaseous toxicity.
- $Cu_2O$-M/$Cu_2O$-L enhanced flame retardancy of UPR.

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## ABSTRACT

Cuprous oxide ($Cu_2O$) as an effective catalyst has been applied to enhance the fire safety of unsaturated polyester resin (UPR), but the particle size influence on combustion behaviors has not been previously reported. Herein, the UPR/$Cu_2O$ composites (metal oxide particles with average particle-size of 10, 100, and 200 nm) were successfully synthesized by thermosetting process. The effects of $Cu_2O$ with different sizes on thermostability and combustion behaviors of UPR were characterized by TGA, MCC, TG-IR, FTIR, and SSTF. The results revel that the addition of $Cu_2O$ contributes to sufficient decomposition of oxygen-containing compounds, which is beneficial to the release of nontoxic compounds. The smallest-sized $Cu_2O$ performs the excellent catalytic decomposition effect and promotes the complete combustion of UPR, which benefits the enhancement of fire safety. While the other additives retard pyrolysis process and yield more char residue, and thus the flame retardancy of UPR composites was improved. Therefore, catalysis plays a major role for smaller-sized particles during thermal decomposition of matrix, while flame retarded effect became gradual distinctly for the larger-sized additives.



## 1. Introduction

Nanosized materials, such as metal and their oxides, have widely attracted attention in industrial applications on account of their specific physical and chemical properties [1,2]. Nano-$Cu_2O$ has been widely exploited for use in the fields of photocatalyst [3], solar energy conversion [4], antifouling coatings [5], and water-splitting materials [6]. $Cu_2O$ is the subject of considerable interest because it is a p-type semiconductor with a direct band gap of 2.0-2.2 eV [7], which makes it a promising material as solar converter [8]. Despite of electrode, $Cu_2O$ is also applied as a catalyst for several important oxidation reactions. For example, more than 99.5% conversion of CO to $CO_2$ could be achieved by $Cu_2O$ nanoparticles supported on silica gel [9]. In addition, it is nontoxic, abundantly available, environmentally friendly and easily prepared. $Cu_2O$ can be successfully synthesized by many methods including electrolysis [10], reduction of cupric salts or copper oxide [11], thermal oxidation [12], and hydrothermal production [13].

Many works have indicated that modification of polymeric materials with nanosized fillers is attractive, which could effectively improve the performance of polymers for a variety of applications [14–16]. For example, a chemiresistive sensor for chemical warfare agents, composed by single-walled carbon nanotubes (SWCNTs) and polythiophene, widens the application of polymer as receptor [17]. Nanosized metallic oxides are also used as modifying agents for polymers. Core-shell polyamide/$Fe_3O_4$ magnetic nanoparticles exhibited superparamagnetic properties above the blocking temperature, which indicated that the magnetic hyperbranched aromatic polyamides nanoparticles obeyed a single-domain theory [18]. However, the inherent flammability limits many potential applications of polymers for safety considerations. Fire retardation of polymers can be achieved through the use

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of fire retardants (FRs), including metallic oxide. The presence of the metallic oxides (such as $ZrO_2$, $MoO_3$, and $Cr_2O_3$) could raise the amount of residue of styrene butadiene rubber/intumescent flame retardant composites and decrease the value of heat release rate (HRR), improved the flame retardancy of composites [19]. Nano-sized ferric oxide was introduced into methysilicone resin (MSR) for enhancing the thermostability. The thermogravimetric analysis (TGA) results show that $Fe_2O_3$ nanoparticles can remarkably improve the thermal stability of MSR [20]. The catalytic effect of $Cu_2O$ has also been studied on the degradation processes of polymers [21,22]. The influence of a variety of metal oxides on thermal behaviors of polymers has been studied extensively. Rare researches about the effect of particle size have been reported.

Unsaturated polyester resins (UPRs) are extensively used in composite industries including aerospace, automotive, marine and load-bearing infrastructure because of their excellent ease of processibility, outstanding chemical resistance, good mechanical properties and lost cost [22,23]. However, fire hazards have seriously hindered the commercial application of UPRs. Large quantities of smoke and toxic gases are produced during combustion procedure, which is harmful to environment and human health. So the increasing commercial utilization demands the development of effective and environmental friendly flame retardants to enhance fire safety. Due to non-toxicity and flame retardant efficiency, nanoscale inorganic compounds have been applied to reduce the fire hazards of polymers [24,25].

In this work, nanoscale $Cu_2O$ with different sizes are successfully synthesized and introduced into UPR to study their influence on thermal behaviors of UPR. Based on the previous investigation, we proposed to fabricate the $Cu_2O$ by a facile and efficient wet chemical method. $Cu_2O$ with different particle size means different superficial area, which has a great influence on catalytic effect [26,27]. It is reasonable to expect that different $Cu_2O$ sizes could affect the degradation process of polymers in varying degrees. With appropriate characterization methods, it is anticipated that the effects can be studied comprehensively and possible impact mechanism can be proposed.

## 2. Experimental section

### 2.1. Materials

Copper sulfate, sodium borohydride, polyvinyl pyrrolidone (PVP), and benzoyl peroxide (BPO) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Unsaturated polyester (UPR, commercial name 196) with a styrene content of 38 wt% was supplied by Hefei Chaoyu Chemical Co. Ltd.

### 2.2. Synthesis of $Cu_2O$

A fixed mass ratio (4:1) of copper sulfate and PVP were dissolved in 1.4 L distilled water with magnetic stirring. The pH of obtained solution was regulated to ~9 using a standardized sodium hydroxide solution (0.1 M). The solution was continued stirring for 0.5 h before adding stoichiometric sodium borohydride. Then the reaction system was vigorously agitated for another hour. Precipitate was collected, washed and vacuum drying overnight at 50 °C. In this work, $Cu_2O$ were synthesized with different mass of copper sulfate (0.08, 0.4 and 0.8 g) and named as $Cu_2O$-S, $Cu_2O$-M and $Cu_2O$-L, respectively.

### 2.3. Synthesis of UPR/$Cu_2O$ composites

UPR/$Cu_2O$ composites samples were prepared by solidification process with recrystallized BPO. In general, as-prepared $Cu_2O$ was ultrasonic dispersed in a certain volume of pre-polymer to yield a homogeneous dispersion. The calculated BPO was dissolved in the dispersion and then cast the mixed solution into molds, cured at 70 °C for 3 h, and post cured at 120 °C for 4 h.

### 2.4. Characterization

X-ray diffraction (XRD) measurements were performed on a Japan Rigaku D Max-Ra rotating anode X-ray diffractometer equipped with a Cu-$K_\alpha$ tube and a Ni filter ($\lambda$=0.1542 nm). The scanning rate was 4° $min^{-1}$ and the range was 10–70°.

The morphology and structure of $Cu_2O$ and fractured surfaces of UPR composites were studied by a PHILIPS XL30E scanning electronic microscope (SEM). Transmission electron microscopy (TEM, JEM-2100F, Japan Electron Optics Laboratory Co., Ltd.) was employed to investigate the micro-morphology of $Cu_2O$.

TGA was performed on a TGA Q5000IR (TA Instruments, USA) thermo-analyzer instrument from 30 to 700 °C at a heating rate of 20 °C $min^{-1}$ under an air or nitrogen flow of 60 mL $min^{-1}$. Samples of about 5.0 mg were measured in an alumina crucible.

Microscale combustion calorimetry was used to investigate the flammability characteristics of UPR composites according to ASTM D7309-07. Samples of about 5 mg were heated in nitrogen atmosphere at a constant heating rate of 1 °C $s^{-1}$ from room temperature to 650 °C. The decomposition products were mixed with oxygen (20 mL $min^{-1}$) and then combusted in the combustion furnace (900 °C).

RTIR spectra were obtained from a Nicolet 6700 spectrometer (Nicolet Instrument Corporation, USA). The samples were mixed with KBr powders and pressed into tablets for characterization with the transmission mode.

TG-IR was conducted using a TGA Q5000IR thermogravimetric analyzer that was linked to a Nicolet 6700 FTIR spectrophotometer. About 5–10 mg of the sample was put in an alumina crucible and heated from 30 to 700 °C. The heating rate was 20 °C $min^{-1}$ (nitrogen atmosphere, flow rate of 30 mL $min^{-1}$).

Laser Raman spectroscopy (LRS) measurements were carried out at room temperature with a SPEX-1403 laser Raman spectrometer (SPEX Co., USA) with excitation provided in backscattering geometry by a 514.5 nm argon laser line.

The SSTF tests were measured according to ISO TS 19700 [28–30]. Typically, 20 g of samples, loaded into the quartz boat, is fed into the furnace at 650 °C at around 40 mm $min^{-1}$. By the primary air flow rate with 10 L $min^{-1}$ and second air flow rate with 40 L $min^{-1}$, oxygen depletion and yields of carbon dioxide, carbon monoxide, and smoke intensity were determined using standalone detectors.

## 3. Results and discussions

### 3.1. Structural and morphology characterization of $Cu_2O$

Typical XRD spectra of $Cu_2O$ were showed in Fig. 1a [31]. The similar XRD curves indicate that the increasing concentration of reaction compounds made little change in the crystal form of prepared $Cu_2O$. $Cu_2O$ has been identified to be stable at limited ranges of temperature under $N_2$ atmosphere. But under air conditions, with a sufficiently long oxidation time, $Cu_2O$ will be oxidized into CuO [32]. The thermal oxidation of synthesized $Cu_2O$ was investigated by TGA, as showed in Fig. 1b. The slight weight loss of $Cu_2O$ under $N_2$ atmosphere is resulted in the decomposition of PVP, which may retains on the surface of $Cu_2O$ particles. More than 10% weight gain under air conditions suggests $Cu_2O$ is oxidized into CuO.

The particle morphology and structure were further investigated by SEM, TEM and HRTEM. Particle size of $Cu_2O$ increases with