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# Comparative investigation on combustion property and smoke toxicity of epoxy resin filled with α- and δ-$MnO_2$ nanosheets

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ABSTRACT

Manganese dioxide ($MnO_2$) as a promising green material has attracted widely attention in virtue of its outstanding chemical and physical properties. Herein, $MnO_2$ nanosheets with α- and δ- crystal structures were used to comparatively study the influence of crystal structures on the fire resistance of EP resin. Cone calorimeter results confirmed that δ-$MnO_2$ nanosheets achieved better improvements than α-$MnO_2$ nanosheets in reducing the PHRR and THR values as well as suppressing smoke release during combustion process. Moreover, Raman data and SEM tests showed that δ-$MnO_2$ nanosheets could effectively promote the char dense of char residues of EP composites. TG-IR results also indicated that the pyrolysis toxic products were significantly decreased after the incorporation of δ-$MnO_2$ nanosheets. By the way, the mechanical property of EP/δ-$MnO_2$ 2% composites had no obvious reduction compared with pristine EP resin, which would not restrict the application of EP resin in fields requiring high mechanical properties.



## 1. Introduction

Epoxy resin (EP), as a vital thermosetting polymer matrix, has been applied in the fields of adhesive [1], insulation devices [2,3] and printed circuit board [4,5] in virtue of its excellent mechanical properties, be resistant against solvent corrosion and excellent electrical insulation. However, the application of EP resin has been badly limited due to its high flammability. As we know, EP can be easily ignited and thereby produces large amount of heat and smokes, which are the main reasons for permanent injury and death in fire accidents [6]. So, it is of great significance to reduce the production of heat and smokes of EP resin when fire occurs.

Up to now, nano-scale fillers such as layered double hydroxides [7,8], carbon nanotubes [9], montmorillonite [10] and graphene [11–15] have attracted considerable attention by researchers and utilized to improve the fire safety of EP due to the low addition. Among them, layered-like structure materials are primarily dependent on the physical barrier effect to delay the release of heat and pyrolysis products, thus improving the flame retardancy of EP resin. One-dimensional materials are mainly by the formation of networks to retard the transfer of heat and smoke [16,17]. Nanoparticles such as Zinc hydroxystannate and titanium dioxides can promote the catalytic charring and form dense char layers to slow down the decomposition process [18–21]. Usually, physical barrier effects from layered structure can perform better than one-dimensional and three-dimensional structures.

In our previous work, Manganese dioxide ($MnO_2$) with different morphologies are employed to improve the fire safety of EP [22]. It was proved that $MnO_2$ with different crystalline structure can promote the catalytic charring and $MnO_2$ with a layered structure performed the best in improving the fire safety of EP among different morphologies. However, $MnO_2$ nanosheets with different crystalline structures have not been studied. Moreover, the investigation of mechanical property is limited. Therefore, it is of necessary to further investigate the influence of $MnO_2$ nanosheets with different crystalline structures on the fire safety and mechanical property of EP resin.

In this work, $MnO_2$ nanosheets with α and δ crystalline structures are synthesized and act as nano-fillers incorporated into EP matrix for better fire safety. The thermal stability and flame retardancy of EP composites is evaluated by thermogravimetric analysis and cone colorimeter tests. Pyrolysis products are studied by thermogravimetric infrared. Mechanical properties of pure EP and its composites are investigated by dynamic mechanical analysis.

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## 2. Experimental section

### 2.1. Raw materials

All chemicals were of analytical grade and used as received without further purification. Potassium permanganate ($KMnO_4$), oleic acid, $MnCl_2$ $4H_2O$, TMAOH (25 wt% in $H_2O$), ethyl acetate and acetonitrile were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Bisphenol-A type EP was purchased from Shixian Chemical Industry Co., Ltd. A curing agent (diaminodiphenylmethane) and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd.

### 2.2. Synthesis of α and δ-$MnO_2$ nanosheets

The synthesis of α-$MnO_2$ was according to our previous works [23]. In a typical process, 40 mL of mixed aqueous solution prepared from 12 mL of 1.0 M tetramethylammonium hydroxide (TMAOH), 2 mL of 30 wt% $H_2O_2$ and 16 mL of deionized water was poured into 20 mL of 0.3 M $MnCl_2$ aqueous within 15 s. The resulting dark brown suspension was stirred overnight in an open atmosphere at room temperature. Then, the obtained suspension was separated by filtration and washed with copious amount of deionized water and finally dried at 80 °C. For δ-$MnO_2$ [24], 15 mmol of $KMnO_4$ was completely dissolved in 750 mL deionized water. Then, 200 mL of ethyl acetate was added into the above solution by constantly stirring. The solution was maintained at 95 °C and refluxed overnight. The obtained brown product was filtrated and washed with deionized water and ethanol consecutively, thereby dried at 80 °C for further use.

### 2.3. Preparation of EP/α-$MnO_2$ and EP/δ-$MnO_2$ nanocomposites

EP nanocomposites was prepared according to the procedure described in our previous report [22]. Typically, 1.22 g of $MnO_2$ was put into 50 mL acetone by ultrasonication and stirring to form a homogeneous suspension. 50 g of the pre-melting EP was poured into the above suspension under mechanical stirring and maintained over 6 h. Then, the suspension was heated at 100 °C for 12 h under constant stirring to remove the solvent. Thereafter, 10 g of pre-melting 4, 4′-diaminodiphenylmethane was added into the mixture under stirring. Lastly, EP nanocomposites can be obtained after cured at 100 °C and 150 °C for 2 h, respectively.

### 2.4. Characterization

X-ray diffraction (XRD) measurements were performed using a Japan Rigaku D = Max-Ra rotating anode X-ray diffractometer equipped with a Cu K a tube and Ni filter (k = 0.1542 nm).

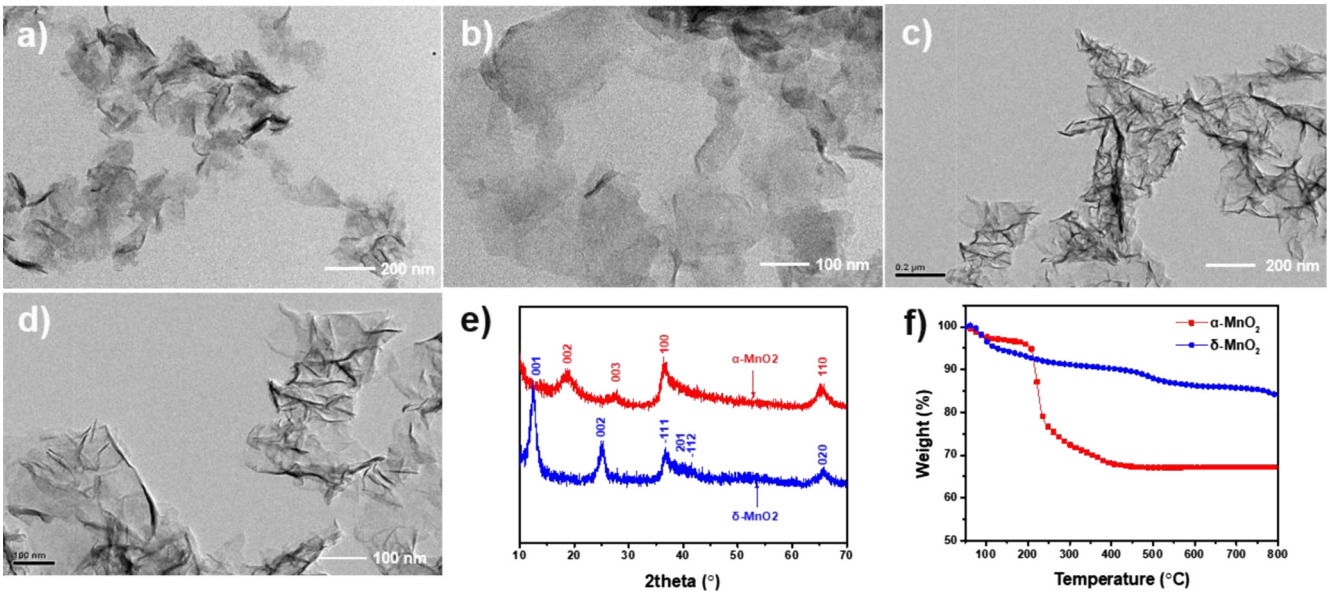


**Fig. 1.** TEM images of (a, b) α-$MnO_2$ and (c, d) δ-$MnO_2$; (e) XRD pattern and (f) TGA data of α-$MnO_2$ and δ-$MnO_2$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

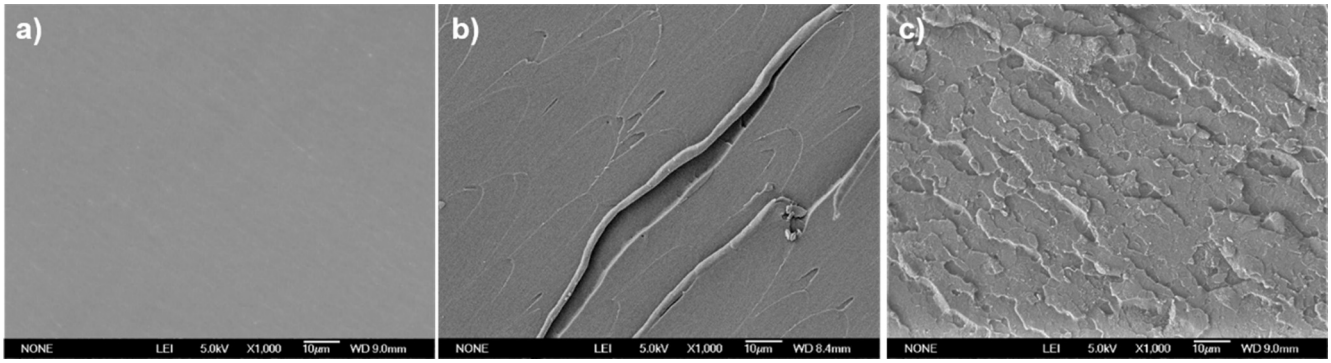


**Fig. 2.** SEM images of fracture surfaces cryogenically broken after immersion in liquid nitrogen for (a) pure EP, (b) EP/α-$MnO_2$ 2% and (c) EP/δ-$MnO_2$ 2%.