Investigation of the characteristics of gaseous formaldehyde emission from synthetic rubbers assisted by S-TiO$_2$ catalyst

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Abstract. Gaseous formaldehyde emission from synthetic rubbers was simulated using a 60-L environmental chamber to explore the effect of different rubbers on formaldehyde emission. The formaldehyde emission factor (EF) of synthetic rubbers was more likely to exceed the limit for mixed type, which was mainly attributed to the quality of the adhesives in raw materials. Furthermore, the emission characteristics of mixed-type rubbers in small chambers were obtained. EF rapidly increased, especially during the inception stage, and then its rate of increase slowed, reaching a peak at approximately 4-5 h. The relative standard deviations of EF were within 5% when the measurement was extended to 13 h. This method can be used to monitor volatile hazardous substances emanating from synthetic rubbers, providing a theoretical basis for corresponding supervision. In addition, to degrade the background values in chambers, the photo-induced reactions were catalyzed with S-doped TiO$_2$ under visible light, as this helped to shorten the pre-treatment time of the air in the chamber.

1. Introduction

With the development of synthetic materials, synthetic rubbers currently not only allow year-round sports but also have good elasticity, anti-skid properties and wear resistance [1-3]. Synthetic rubbers appear in many basic sports facilities such as schools’ track and field, basketball courts, football pitches and park playgrounds. Formaldehyde, which exists in colour powders and other synthetic material components, is listed by the World Health Organization as a potential carcinogen [4]. The toxic effects of formaldehyde on humans mainly manifest as nervous and respiratory system symptoms, often resulting in allergic dermatitis or chronic respiratory diseases. Moreover, a high level of exposure to formaldehyde may cause immune dysfunction and leukaemia [5].

In recent years, the issue of harmful substance emissions from synthetic rubbers has caused growing concerns globally [6-8]. Formaldehyde emission is mainly affected by environmental factors such as temperature, relative humidity (RH) and air velocity [9]. To achieve rapid construction by reducing the viscosity of glue, organic solvents containing formaldehyde are often used in surface constructions [10]. As one of the representative pollutants, formaldehyde negatively affects the body when it is inhaled or comes into contact with the skin [11,12]. It is more volatile under high temperatures, and the temperature of synthetic materials is greater than or equal to 60 °C in hot weather. To the best of our knowledge, there are no available reports in the literature concerning
formaldehyde emissions from synthetic rubbers. Therefore, a study on these emissions to simulate the real circumstance of rubbers is necessary and has potential social benefits.

In this study, S-doped anatase TiO₂ (S-TiO₂) was prepared using a hydrothermal process and post-calcination. In an environmental chamber, the visible-light degradation of the volatile organic compounds was conducted using S-TiO₂ to decrease the background interference and shorten the pretreatment time. Using small chambers for simulation, the gaseous formaldehyde from synthetic rubbers and the emission factor (EF) of different types of rubber were analysed. In addition, the emission characteristics of formaldehyde in mixed type were examined, together with the reasons for the high formaldehyde levels.

2. Materials and methods

2.1. Instruments and chemicals

The instruments used included an XBN-6LT60 environmental test chamber (China), an Agilent Cary 300 UV-Vis spectrophotometer (USA), a Talboys magnetic hotplate stirrer (USA), a Rigaku Ultima IV X-ray diffractometer (Japan), a Mettler Toledo SevenExcellence pH meter (Switzerland), and a JEOL JEM-2100F transmission electron microscopy (Japan). A Yamato FO110C muffle furnace (Japan), a Talboys 2804 HEAT STIR magnetic hotplate stirrer (USA), an AMAE EM-1500 intelligent air sampler, an Eagle View Electronic Technology 80 W LED lamp, a Bomex large bubbling absorber, and a DragonLab Flat Spin ultrathin magnetic stirrer were also utilized.

Analytical-grade titanium butoxide, thiourea, acetylacetone, ammonium acetate, acetic acid and ethanol were purchased from Macklin Biochemical (China). We obtained 0.25% acetylacetone by treating with a certain proportion of ammonium acetate/water/glacial acetic acid/acetylacetone media. 1000 mg L⁻¹ formaldehyde standard solution was purchased from TMRM (China), and the different concentration standards were prepared by diluting with purified water (resistivity of 18.2 MΩ cm) prepared using a Milli-Q integral ultrapure water system (USA).

2.2. Synthesis of S-TiO₂ and characterization

S-TiO₂ is considered a promising photocatalyst because of its non-toxic, stable chemical properties and no secondary pollution [13]. To synthesize the catalyst powder, 250 mL ethanol (as a solvent), 32.8 mL titanium butoxide (as a Ti source) and 9.0 g thiourea (as a S source) were added in a beaker with stirring. The mixture was subjected to ultrasonic treatment for 30 min until the constituents were completely dissolved, and the pH of the solution was adjusted to 6.0. Next, the liquid was transferred to a 400 mL Teflon-lined hydrothermal reactor and stirred at 150 °C for 7 h [2]. The precipitates were washed with ethanol and water, and then dried in an oven at 70 °C for 1 h. The precursors were calcined in a muffle furnace at 500 °C for 4 h to obtain S-TiO₂.

X-ray diffraction (XRD) analysis was performed using Cu-Kα radiation (λ = 1.5406 Å) with a Cu X-ray tube. Jade software was used to measure the half-maximum bandwidth and the diffraction angle of the diffraction peak. Catalyst particles were scattered in ethanol by ultrasonic dispersion for 5 min, and then used to prepare wafers 3 mm in diameter. The wafers were placed on a copper mesh, and Digital Micrograph software was used to measure the lattice spacings of S-TiO₂ from transmission electron microscopy (TEM).

2.3. Photodegradation of background formaldehyde in environmental chamber

To degrade background values in the chamber, the photoinduced reaction was catalyzed with S-TiO₂ under visible light. S-TiO₂ powder (0.15 g) was re-suspended in 30 mL purified water by ultrasonic treatment for 5 min, and the suspensions were then added to a quartz container using an ultrathin magnetic stirrer. The container was placed at the centre of the chamber and the reaction was commenced by illumination with LED light for 30 min. The degradation rate (Dₜ, %) of formaldehyde is calculated by the following equation:
\[
D_f = \frac{A_0 - A_t}{A_0} \times 100\%
\]  

(1)

where \(A_0\) and \(A_t\) are the absorbance of solution before and after irradiation.

2.4. Preparation of synthetic rubbers and sampling conditions

Different batches of synthetic material specimens were randomly selected from construction companies in China and stored under the following conditions: temperature of 25 ± 1 °C, and 40 ± 2% RH. Before processing the specimens in chambers, their inner surfaces were cleaned with water. Each specimen was cut to a size of 16 × 16 cm (cutting at least 1 cm from the edge of the specimen) and sealed with aluminium foil tape at the artificial cutting edges and the bottom (Figure 1). After the specimens were prepared, the synthetic rubbers were placed in chambers for testing within 1 h.

![Figure 1. Diagram of aluminum foil tape preparation for synthetic rubbers.](image)

To evaluate the formaldehyde emissions from the synthetic rubbers in hot weather, the sampling parameters, including sample loading factor, temperature, RH and atmospheric pressure inside the chamber were set to outdoor conditions (Table 1). The chamber air was then collected for analysis.

**Table 1.** Sampling conditions in environmental chambers.

| Parameters                        | Conditions |
|-----------------------------------|------------|
| Chamber volume \((V)\)            | 60 L       |
| Sample area \((S)\)               | 0.024 m\(^2\) |
| Sampler sorbent                   | Large bubbling absorber |
| Air flow rate                     | 0.2 L min\(^{-1}\) |
| Total sampling volume             | 4 L        |
| Air change rate \((AC)\)          | 0.5 h\(^{-1}\) |
| Sample loading factor \((S/V)\)   | 0.43 m\(^2\) m\(^{-3}\) |
| Surface air velocity              | 0.1 m s\(^{-1}\) |
| Atmospheric pressure \((P)\)      | 102.0 kPa  |
| Temperature \((T)\)               | 60 ± 1 °C  |
| RH                                | 40 ± 2%    |
| Visible-light wavelength          | 410 nm     |
3. Results and discussion

3.1. Size and phase of S-TiO2 nanoparticles

S-TiO2 fabricated by controllable hydrothermal steps appeared crystalline and partially aggregated (Figure 2A). The average grain size of S-TiO2 was 14 nm, similar to that of the (101) diffraction peak calculated by the Scherrer equation. The lattice spacing was 0.35 nm, corresponding to the (101) crystal plane of the high-resolution TEM observation (Figure 2B), respectively, which was considered as the crystal plane of the anatase phase.

Figure 2C and 2D show the energy dispersive X-ray (EDX) spectrum obtained by micro-area elemental analysis and the XRD pattern of S-TiO2, respectively. The chemical compositions were S, Ti and O, and the Cu peak was attributed to the copper mesh. Based on JCPDS No. 89-4921, the crystal was in the anatase phase. The peaks at 25.3°, 37.9°, 38.6°, 48.1°, 54.1°, 55.0°, 62.8°, 68.9°, 70.3°, 75.2° and 76.1° were assigned to the diffraction from (101), (004), (112), (200), (105), (211), (204), (116), (220), (215) and (301) crystal planes of the anatase phase, respectively.

Figure 2. TEM image (A), high-resolution TEM image (B), EDX spectrum (C) and XRD pattern (D) of S-TiO2.

3.2. Monitoring results of formaldehyde emission from synthetic rubbers

A calibration curve with formaldehyde in the range of 0.0–2.0 μg was prepared; the absorbance exhibited good linear relation with the known amount of standards ($A = 0.203C + k$). After the photodegradation of formaldehyde in an environmental chamber, 5 mL liquor extract from a large bubbling absorber (centrifuged at 1500 rpm and filtered through a hydrophilic membrane) was evenly blended with 0.25% acetylacetone and then heated in boiling water. This was then placed in a quartz cuvette (pure water was set as the reference solution) and the absorbance was measured. The
The absorbance of the background formaldehyde was detected by a UV-Vis spectrophotometer at a wavelength of 415 nm. S-TiO2 enhanced the Df of the residual formaldehyde in the chamber (Figure 3). Because Df was ≥96%, this increased the efficiency of the pre-preparation, saving approximately 4 h and avoiding disturbance in the emission test.

*Figure 3. Schematic of formaldehyde photodegradation in environmental test chambers.*

| No. | A_i  | T (°C) | C_i (mg m⁻³) | C_si (mg m⁻³) | EF (mg m⁻² h⁻¹) |
|-----|------|--------|--------------|--------------|-----------------|
| 1   | 0.020| 60.4   | 0.004        | 0.005        | ND²             |
| 2   | 0.557| 59.3   | 0.269        | 0.320        | 0.801           |
| 3   | 0.058| 60.8   | 0.023        | 0.027        | 0.068           |
| 4   | 0.019| 60.7   | 0.003        | 0.004        | ND              |
| 5   | 0.509| 60.2   | 0.245        | 0.293        | 0.730           |
| 6   | 0.076| 60.0   | 0.032        | 0.038        | 0.094           |
| 7   | 0.145| 59.3   | 0.066        | 0.078        | 0.195           |
| 8   | 0.299| 59.2   | 0.141        | 0.168        | 0.421           |
| 9   | 0.063| 60.6   | 0.025        | 0.030        | 0.075           |
| 10  | 0.268| 60.0   | 0.126        | 0.150        | 0.379           |
| 11  | 0.051| 60.9   | 0.019        | 0.023        | 0.058           |
| 12  | 0.071| 60.2   | 0.029        | 0.035        | 0.087           |
| 13  | 0.042| 60.7   | 0.015        | 0.018        | 0.044           |
| 14  | 0.887| 59.3   | 0.431        | 0.514        | 1.283           |
| 15  | 0.064| 60.5   | 0.026        | 0.031        | 0.077           |
| 16  | 0.097| 59.9   | 0.042        | 0.050        | 0.125           |
| 17  | 0.053| 60.1   | 0.020        | 0.024        | 0.060           |
| 18  | 0.030| 60.9   | 0.009        | 0.011        | ND              |
| 19  | 0.826| 60.8   | 0.401        | 0.480        | 1.199           |
| 20  | 0.077| 60.3   | 0.032        | 0.038        | 0.096           |

*Table 2. Summary of formaldehyde emission parameters for synthetic rubbers.a*

a The instrument detection limit of formaldehyde is 0.027 mg m⁻² h⁻¹.

b ND = Not detected.
To monitor the emission parameters of formaldehyde in the chamber, it was necessary to control the temperature, RH and surface air velocity [14]. The formaldehyde concentration \((C_i)\) and formaldehyde concentration in a standard state \((C_{si})\) were examined in six small chambers using different sequence numbers. The \(EF\) values of the different rubbers were calculated (Table 2). \(C_i\) is calculated by Equation (2):

\[
C_i = \frac{A_i - k}{0.203 \times 4}
\]

where \(A_i\) is the absorbance of the sample solution, \(k\) is the constant of linear regression equation, and 4 is the sampling volume (L).

\(C_{si}\) and \(EF\) can be calculated by Equations (3) and (4):

\[
C_{si} = C_i \times \frac{101.3}{P} \times \frac{T + 273.15}{273.15}
\]

\[
EF = \frac{C_{si} \times V \times AC}{S}
\]

Six of the tested batches were \(>0.3\) mg m\(^{-2}\) h\(^{-1}\) (Table 3). Of these, two batches, including No.8 [ethylene propylene diene monomer (EPDM)] and No.10 [polyurethane (PU)] were approximately 0.4 mg m\(^{-2}\) h\(^{-1}\). The \(EF\) values of No.2, No.5, No.14 and No.19, which were mixed-type rubbers, were \(>0.7\) mg m\(^{-2}\) h\(^{-1}\). By evaluating the remaining 14 batches, we found that they were environmentally friendly. To examine the presence of formaldehyde in the mixed type, we considered a three-step method from the perspective of the production process. First, an appropriate amount of granules was added to adhesives. Second, 8-mm- and 2-mm-thick adhesives were successively applied to the bottom of the rubber, which was then covered with a layer of liquid cement spray. An important factor regarding formaldehyde emissions is that all the three steps involved an adhesive. A follow-up test was performed to ensure the physical properties of No.8 and No.10, and the \(EF\) of the finished products was \(<0.1\) mg m\(^{-2}\) h\(^{-1}\) after proper ventilation and sun exposure. Because urea-formaldehyde and phenol-aldehyde are common organic solvents, lots of rubber products contain formaldehyde. This demonstrates that the \(EF\) of synthetic rubbers is considerably affected by the adhesives in raw materials.

### Table 3. Comparison of \(EF\) from synthetic rubbers.

| No. | \(EF\) (mg m\(^{-2}\) h\(^{-1}\)) | Type of rubbers            |
|-----|---------------------------------|-----------------------------|
| 2   | 0.801                           | 13 mm-thick seepage rubber  |
| 5   | 0.730                           | Composite silicon-modified PU|
| 8   | 0.421                           | Sulfonated EPDM             |
| 10  | 0.379                           | Flexible PU                 |
| 14  | 1.283                           | Synthetic copolymer rubber  |
| 19  | 1.199                           | 13 mm-thick breathable rubber|

#### 3.3. Characteristics of formaldehyde emission from mixed-type rubbers

We screened the positive formaldehyde specimens and the \(EF\) curves of the mixed-type rubbers. The gaseous formaldehyde was extracted from the chamber air. The error bars correspond to the standard deviations (\(n = 3\)). When the relative standard deviations of \(EF\) were within 5\%, for long-term emissions, we considered this the steady-state [15,16].

\(EF\) increased rapidly during the initial stage, indicating that the 13-mm-thick breathable rubber and composite EPDM reached a peak after approximately 4 h, while the peak of the composite silicon-modified PU was reached after approximately 5 h. The decreasing tendencies then gradually slowed and the curves decreased in a non-linear manner. When the measurement was extended to 13 h, the \(EF\)
values were stable with only small fluctuations. This was primarily because the thermal motion of formaldehyde was accelerated when the specimens were transferred from 25 ± 1 to 60 ± 1 °C, and the molecule desorption action was strengthened. As free formaldehyde spread into the air, its diffusion decreased slowly. In particular, a comparison of $EF$ in Figure 4 indicates that the greater the emissions in the initial stage, the higher the final balance value. Accordingly, these experimental data further improve the scientificity of formaldehyde monitoring in environmental chambers.

![Graph](image)

**Figure 4.** Variation of formaldehyde emission factors from representative mixed-type rubbers: (a) 13 mm-thick breathable rubber; (b) composite EPDM; (c) composite silicon-modified PU.

### 4. Conclusions

This study investigated the gaseous formaldehyde emitted from representative synthetic rubbers and the emission characteristic of formaldehyde using small environmental chambers with colorimetric detection at 415 nm. 14 nm S-TiO$_2$ was used as a catalyst under visible light for 30 min, which considerably enhanced the photodegradation of the background formaldehyde. Results show that mixed-type rubbers are more likely to release formaldehyde, and the addition of low-quality raw material adhesives during the production process promotes formaldehyde emission. The $EF$ peak of the mixed-type rubbers occurs at around 5 h. An equilibrium state for formaldehyde emission is obtained after 13 h. Hence, an accurate evaluation of formaldehyde emissions from synthetic materials is not only appropriate to improve the quality of synthetic materials but also as a critical step in formaldehyde monitoring.

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