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Visualization Research on Hydrothermal Process of Polyoxymethylene Particle: Swelling and Dissolving

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With the rising concerns on environmental pollution and emission reduction, plastic waste disposal draws great attention from governors and scientists. Instead of landfilling and incineration, chemical treatments are considered less polluting and resources recovering. Hydrothermal processing is considered a prospective technology for this issue. To regulate the conversion process and improve efficiency, a key step is to know the dominant stages and clarify the controlled part of the reaction. However, there is very limited number of researches on the visualized exhibition of this process. In this paper, a hydrothermal process visualization measure is adopted, to intuitionally demonstrate the whole conversion process. Polyoxymethylene (POM) spheres are employed as the feedstock in this experiment. A fixed-focus camera records the plastic sphere particle undergoing three stages of heated, swelling and dissolution, under hydrothermal condition. At the heated stage, the solid sphere becomes transparent, then during the swelling stage, the transparent sphere expands to around 130 % of the original size (sectional area), finally the expanded sphere is dissolved into fragments dispersing in the water. During the hydrothermal conversion, the carbon component of the plastic sphere immigrated into the aqueous phase, carbon recovery rate of the process reached as high as 90 %. The visualized results well demonstrate the physical and chemical transition of hydrothermal process, which would be a promising direction for future study.

1. Introduction

Listed as one of the greatest inventions of the 20th century, plastics occupied an irreplaceable position in almost every aspect of human society (Andrady and Neal, 2009), whose yield and waste volume kept increasing over the past 50 years (Leal Filho et al., 2019). White pollution is notorious for the stability of plastics in nature surroundings, some plastics could exist for decades without degrading. More often, they are decomposed into fragments by the effect of physical forces, chemical erosion and microorganism (Wright and Kelly, 2017), enhancing the ability of adhesion to toxics and migration, which brings more harm to local ecosystem (La Kanhai et al., 2017). Landfilling have been the most common form of waste disposal, bringing risks of chronic toxic exposure to local humans (Palmeri et al., 2012). With the migration and circulation of groundwater, the harm will be aggravated. Thus, circular economy, plastic economy in particular, comes in focus of the scientific community (Dahlbo et al., 2018). The treatments of plastic wastes are usually classified into four routes, primary (re-extrusion), secondary (mechanical), tertiary (chemical), quaternary (energy recovery) (Al-Salem et al., 2009). Primary recycling is the simplest and the most saving route, however, limited by many factors like dyes, contaminants, qualities, etc., only roughly 2 % is closed-loop recycled of all plastics (Pedersen and Conti, 2017). Hydrothermal processing has been proved an effective strategy for tertiary recycling of plastics, different plastics polymers have been studied such as high impact polystyrene (HIPS) (Bai et al., 2019), polypropylene (PP) (Bai et al., 2020), nylon-66 (PA) (Meng et al., 2004), nine kinds of pure plastics Poly(butylene terephthalate) (PBT), Polycarbonate (PC), Poly(ethylene terephthalate) (PET), Poly(lactic acid) (PLA), Poly(methyl methacrylate) (PMMA), Poly(oxymethylene) (POM), Poly(p-phenylene oxide) (PPO), Poly(vinyl alcohol) (PVA), Styrene-butadiene (SB). (Pedersen and Conti, 2017), and plastics waste mixture (Sugano et al., 2009).

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The high solubility, low viscosity, and high diffusibility of hot water provide good reaction conditions for the decomposition of polymers (Kruse and Dahmen, 2015)

As a promising technique for plastics recycling, hydrothermal processing is worth deep studying to improve the conversion efficiency. To investigate the concrete behavior of the solid plastic under hydrothermal conditions, the visualization research was carried out. In this work, a solid POM sphere particle was processed under hydrothermal conditions, which was recorded by a fixed-focus camera for analysis. From the real-time videos, it could intuitionally be observed that the particle was undergoing heated, swelling and dissolving processes.

2. Materials and methods

Polyoxymethylene (POM) sphere particle was employed as the main object, the raw material of which is CE66 by Celanese Corporation. It was chosen for its superior sphericity with a diameter fluctuation of 0.02 % and homogenous density ranging from 1.287-1.384 g/cm^3. POM spheres of 2.5 diameter were employed as feedstocks in this work, the mass weighing data was collected below in Table 1.

The elemental analysis data of POM involved in the experiment was given in Table 2.

Table 1: 25 samples in the total 250 POM spheres of 2.5 mm diameter

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13
(mg)	11.909	11.829	11.839	11.858	11.891	11.859	11.833	11.940	11.822	11.891	11.964	11.954	11.898
	11.822	11.962	11.869	11.952	11.914	11.912	11.881	11.920	11.705	11.910	11.946	11.927	

Table 2: Elemental analysis of POM spheres

Component	C_{ad}	H_{ad}	N_{ad}	S_{ad}	O_{ad}*
Content (%)	40.80	6.751	0.68	0.569	51.2

* Oxygen content was calculated by difference.

Quartz tube reactor involved in this work was of 5 mm inner diameter and 60 mm length, whose measured volume was 1.12 mL. Both the bottom and the top of the sealed tube was spherical, so there is an obvious disparity when considering the tube as a cylinder (theoretical volume is 1.18 mL). As Figure 1 shows that the dimethicone in flask was heated to preset temperature and kept for 1 h, in order to make it a constant temperature system, approximately regarded as Dirichlet boundary condition. Then immediately the tube reactor was put at the heating position in oil bath (Dow Corning pmx-200, 50 cs), the same moment camera was triggered on, the acquisition rate of which (Hikvision MV-CA016-10UM/UC) was set to 60 frames per second (fps). The conversion condition in the tube could refer to the saturated vapor pressure in Table 3.

It is shown in Figure 2, during the image processing part, videos were cut into pictures, each image was acquired every 30 frames from the original video. Each image went through cropped, grayscale, binarized, edge extraction and ellipse detection. Cylinder shaped tube would inevitably bring distortion to the image, therefore, an algorithm was adopted to fix the image by the help of calibration board (18 * 20 square grids, with 0.2 mm side length). After image calibration, the conversion relation was 0.005234 mm/pixel, with a deviation of 0.19 %. In order to fix the POM particle at the proper position so as to carry out image calibration, 300mg zirconium dioxide (ZrO_2) particles were added at the bottom of the tube to support the POM sphere. Before the main research, control experiments were carried out whether the ZrO_2 was added, through TOC (Total Organic Carbon) analysis, this ceramic substance was proved to be not involved in the reaction.

Table 3: Saturated vapor pressure under hydrothermal conditions

Temp. (℃)	200	210	220	230	240	250
P (MPa)	1.55	1.90	2.32	2.80	3.35	3.98

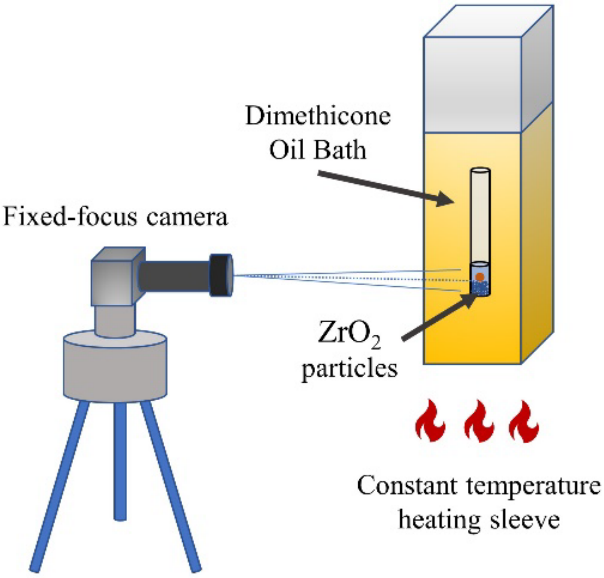

Figure 1: Schematic diagram of the visualization section

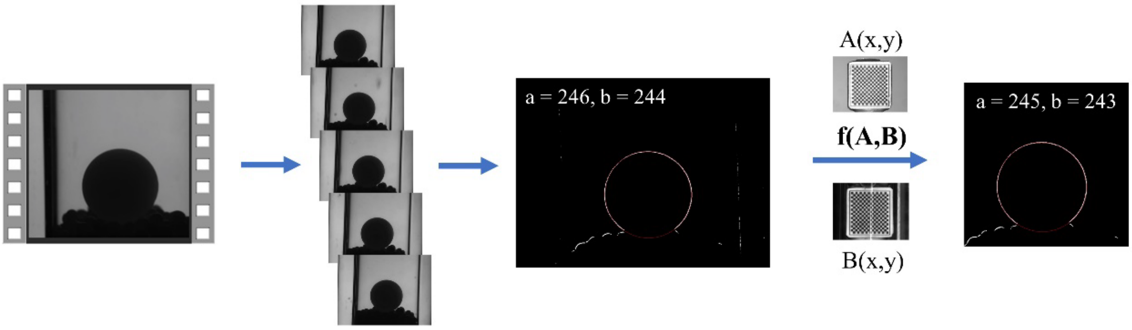

Figure 2: Images processing: (1) video splitting and grey-scale converting; (2) edge extraction;(3) image calibration and cropping (4) ellipse detection (a and b refer to semi-major axis and semi-minor axis (pixels))

3. Results and discussion

As shown in Figure 3, the entire process could be concluded as three stages: heating, swelling, dissolving. At the beginning seconds, the reacting section was on the way to reach the predetermined temperature, the moment that the sphere started to become transparent, could be regarded that the preset temperature was reached. Sequently, the sphere was involved in the stage of swelling, where the sectional area roughly expanded by 30 %. Finally, the sphere began to break into fragments and some fragments were dissolved in the hot water.

To find out the destination of the carbon in plastic, TOC analysis was carried out to check the carbon content in the aqueous phase. The carbon recovery rate (CRR) was evaluated as:

$$CRR = \frac{m_{aq}}{m_{or}} \tag{1}$$

Where: m_{aq} refers to the mass of organic carbon in aqueous phase, m_{or} refers to the mass of carbon content in the original POM sphere.

As shown in Table 4, over 4 mg organic carbon was dissolved in the water after hydrothermal processing while the POM sphere was 1.89 ± 0.058 mg, whose carbon content was measured 40.8 %, which meant the carbon recovery rate of the POM sphere was over 80 % during the hydrothermal conversion. This result was coherent to the claim that the majority of the carbon was recovered in the aqueous phase (Pedersen and Conti, 2017). The results in Table 4 showed under different temperature conditions, the carbon recovery rate remained nearly constant.

After hydrothermal conversion, organic carbon exists in forms of a balance between (unhydrated) formaldehyde and methanediol (Beyler and Hirschler, 2002). In hot water above 200 ℃, the unhydrated form takes the predominant place, while in ambient conditions, the dominant form is methanediol (Matubayasi et al., 2007). This claim remained to be verified in the following study.

Table 4: TOC results of the aqueous phase of hydrothermal processed POM under different temperature conditions (original water dose: 0.2 mL)

(mg)	200 ℃	210 ℃	220 ℃	230 ℃	240 ℃	250 ℃
1	4.8270	4.6858	4.3692	4.4721	4.4370	4.4486
2	4.9517	4.7759	4.5738	4.3602	4.5021	4.1879
3	4.4258	4.2728	4.2354	4.4626	4.1583	4.4786
4	4.3945	4.5390	4.3580	4.5136	4.4434	4.4634
average	4.6498	4.5684	4.3841	4.4521	4.3852	4.3946

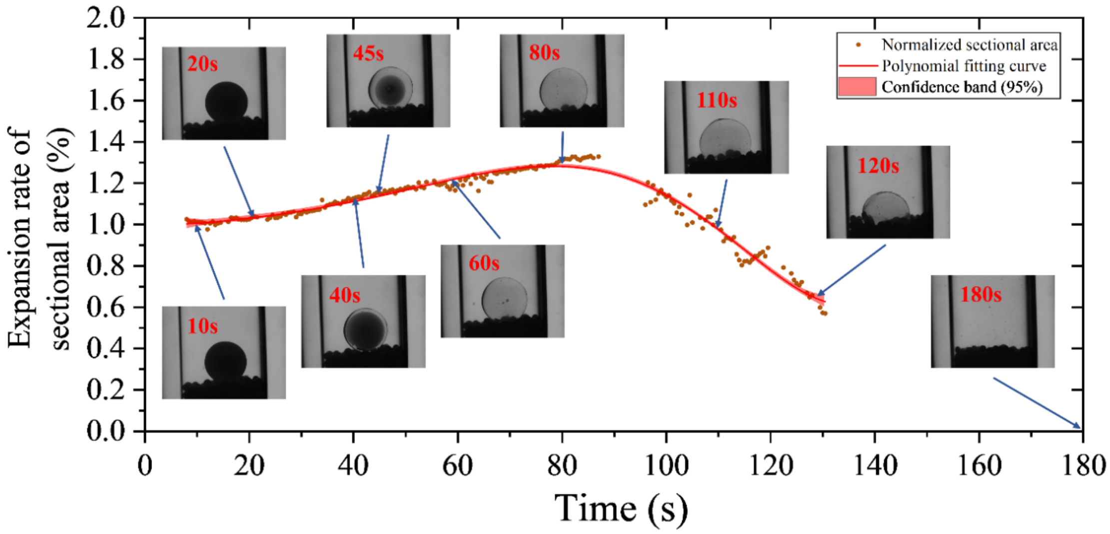

Figure 3: Visualization of entire process of POM sphere in hydrothermal condition (220 ℃, 2.32 MPa)

To clarify the reason why POM sphere expands during the hydrothermal process, experiment was carried out with nigrosine (dye) involved. By the time the POM sphere became transparent and started to expand, the tube reactor was taken out for cooling, then the transparent sphere turned back to solid state. As shown in Figure 4, after dye solution solvothermal processing, the interior of the POM sphere was colored (Figure 4-a), while the one saturated in dye solution under normal temperature condition for 48 hours was not colored (Figure 4-b).

In Figure 4, (a) (b) (c) is the POM sphere treated in ambient condition, (d) (e) (f) is the POM sphere treated under hydrothermal condition (220 ℃, 2.32 MPa). (a) and (d) were carried out in pure water, (b) and (e) were carried out in dye solution, (c) and (f) were the fracture surface of (b) and (e) respectively. Besides of the white scar resulting from cutting, the picture showed the interior of the sphere was colored. It could be proved that, during hydrothermal conditions, small molecules such as water and dye immigrated to the interior of the POM sphere, resulting in the expansion of the volume.

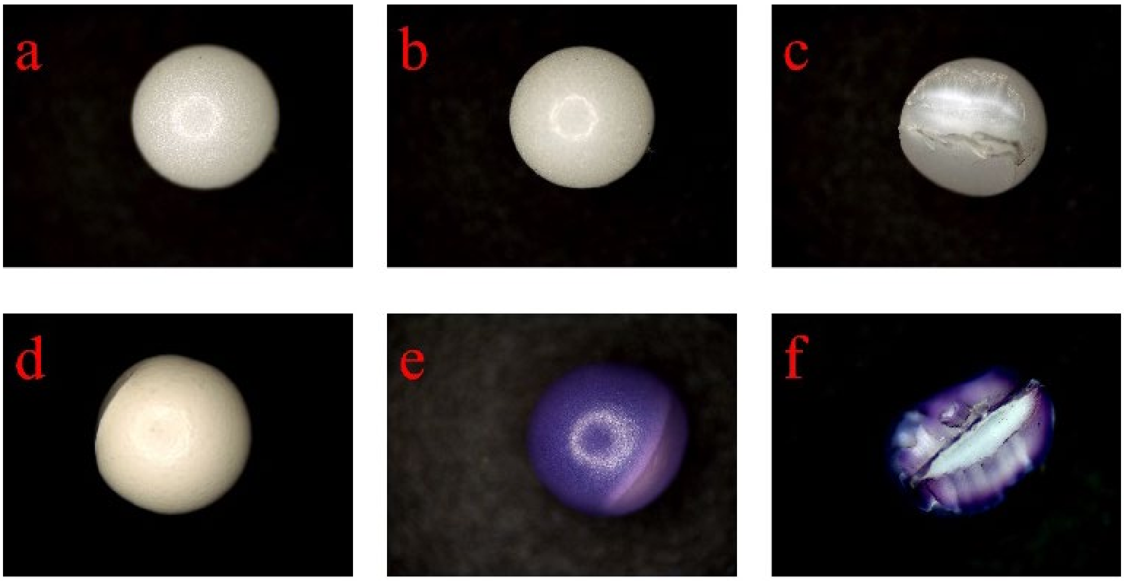

Figure 4: Photos of POM sphere treated in different methods: (a) untreated POM sphere; (b) POM sphere saturated in 1 % nigrosine for 48 h; (c) profile of POM sphere in (b); (d) hydrothermal processed POM; (e) 1 % nigrosine involved hydrothermal processed POM; (f) profile of POM sphere in (e)

4. Conclusion

Under hydrothermal conditions, POM sphere underwent three stages: heating, swelling and dissolving. During the heating stage, the sphere was becoming transparent from the edge of the sphere to the center of it. Then the volume of the sphere started to expand, finally the sphere began to decompose and generate gas, and the viscous state sphere was dissolved in the hot water. With the processing temperature rising (200 - 250 ℃), all the three stages were accelerated, and even conducted simultaneously, but finally the total mass of organic carbon in the aqueous phase were similar, i.e. the recovery rate kept almost constant.

When the temperature of the POM sphere was heated to the preset value, the sectional area of the sphere was getting larger, by approximately 30 %. Through the dyeing experiment and comparison, the results showed the primary cause of the bulk expansion during swelling stage is the solvent migration to the interior of the POM sphere.

The hydrothermal conversion completed in less than 5 minutes (280 s in 200 ℃, 230 s in 210 ℃, 180 s in 220 ℃, 155 s in 230 ℃, 130 s in 240 ℃, 120 s in 250 ℃). TOC analysis results showed that after hydrothermal conversion, the carbon recovery rate was over 80 %. This work visually demonstrates the entire process of the hydrothermal process, proving it a prospective technology for tertiary recycling, and providing a promising direction to clarify the mechanism of high-polymer hydrothermal conversion.

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