



Lipase immobilized on ionic liquid-functionalized magnetic silica composites as a magnetic biocatalyst for production of *trans*-free plastic fats



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ABSTRACT

The main objective of this study is to develop an efficient and environmentally gentle process for production of *trans*-free plastic fats. To achieve this, the core-shell structured magnetic composites were prepared, and then imidazole-based ionic liquids (ILs) were covalently grafted on the magnetic composites. Thereafter, *Candida rugosa* lipase was immobilized on the magnetic IL-functionalized composites. The immobilized lipase could be facilely separated using an external magnetic field. With the magnetic biocatalyst, enzymatic interesterifications of solid palm stearin and liquid rice bran oil blends were performed at 45 °C. It was shown that the total fatty acid (FA) compositions of the binary blends were almost unchanged after the interesterifications, whereas the FA positional distribution and triacylglycerol species were significantly varied. As compared with the physical blends, the interesterified products had a lower slip melting point, and the interesterification could result in an obvious change in the microstructure of the final products.

1. Introduction

Most native vegetable oils have their inherent disadvantages as usually employed in their original forms for the edible food industry, such as poor plasticity, tractility and shortening property (Lee, Akoh, Himmelsbach, & Lee, 2008). During recent years, the consumers preference is towards products containing healthier fat and less fat contents. Therefore, for the purpose of improving the functional characteristics of vegetable oils, the modification method can be used most often to produce new and more valuable oil products with specific properties by varying the compositions of fatty acids (FAs) in native oils, so as to better meet the demand of edible food industry (Xu, 2000). For instance, plastic fats, such as margarine and shortening, are usually produced by the partial hydrogenation of vegetable oils. However, *trans* fats are commonly generated during the partial hydrogenation processes, which have been known to increase the risk factor of coronary heart disease (CHD). Thus, many European countries have banned the use of *trans* fat in food formulations. As recommended by the Food and Agriculture Organization (FAO) and World Health Organization (WHO), *trans* fat content of food should not exceed 4% (Dhaka, Gulia, Ahlawat, & Khatkar, 2011). In this connection, considerable efforts have already been made to develop suitable alternative approaches to produce *trans*-free plastic base stocks for various food applications to replace the traditional hydrogenation process (Costales-Rodríguez, Gibon, Verhé, & De Greyt, 2009). The alternative method as often used

to produce zero-*trans* plastic fat is based on the lipase-catalyzed interesterification between solid fats and liquid oils. Basically, the interesterification can lead to the change of the distribution of FAs on the glycerol backbone of triacylglycerol (TAG) molecules with the formation of new TAG species, which has essentially no possibility to form *trans* FA residues in the end-products (Paula, Nunes, de Castro, & Santos, 2015). Accordingly, the interesterified product can be tailored to meet specific nutritional and functionality requirements by substantially varying the FA composition and altering the FA positional distribution.

Oftentimes, the interesterification is performed by either enzymatically or chemically catalyzed procedures, with a concurrent variation in the textural and functional characteristics of original oils (Costales-Rodríguez et al., 2009). The most commonly used catalysts are metallic sodium, sodium hydroxide and sodium alkoxide, which are efficient, cheap and easy to control in the interesterification processes (Fauzi, Rashid, & Omar, 2013). Unfortunately, these homogeneous catalysts usually suffer from many drawbacks including the need of cleaning process to remove the residual catalyst after the reaction, thereby resulting in undesirable wastewater in the downstream purification processes (Casas, Pérez, & Ramos, 2017). To triumph such weaknesses, enzymatic interesterification has been therefore investigated deeply. In comparison with the chemical catalysts, the major merits of enzymes lie in their selectivity, milder reaction condition, and ease of product recovery (Speranza, Ribeiro, & Macedo, 2015).

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However, the high price of commercial lipases, together with their lack of long-term operational stabilities, has been considered as the main hindrances to the industrial applications for the production of commodity fats in food industry. Nevertheless, such hitches can be minimized by using immobilization techniques, since the immobilized lipase has advantages over free lipase in terms of feasible continuous operations, easy removal from the reaction mixture, simple product purification, and adaptability to industrial biocatalytic processes, hence offering more efficient and cleaner catalytic processes (Jeyarani & Reddy, 2010; Pacheco, Palla, Crapiste, & Carrín, 2013). Over the past decades, the immobilized lipase has been widely utilized for the modification of vegetable oils (Nunes, Pires-Cabral, & Ferreira-Dias, 2011; Xie & Zang, 2016). Specifically, several enzyme immobilization strategies have been explored, such as physical adsorption, covalent binding, physical entrapment and hydrophobic ion pair affinity ligation (Shuai, Das, Naghdi, Brar, & Verma, 2017). Among these methods, the adsorption approach is, by far, the most economical and environmental method in terms of its simplicity of design and low cost, simultaneously maintaining the intact 3D structure of enzymes (Zhai et al., 2010). However, the physical interaction between lipase and porous support is generally not strong enough, thus leading to the leakage of lipase during the biocatalytic processes. In order to address the leaching issues, surface modification of the porous support can be employed to adjust the interactions with the lipase and subsequently improve the stability of the immobilized lipase (Abdullah, Sulaiman, & Kamaruddin, 2009; Zou et al., 2014). It is shown that ionic liquids (ILs) are suitable media for enzymatic catalysis and various lipases were reported to possess excellent activities and extraordinary stabilities in ILs especially as *N*-methylimidazole cation is existed in the ILs (Adak, Datta, Bhattacharya, & Banerjee, 2015; Jia, Hu, Liu, Jiang, & Huang, 2013). In this regard, the surface modification of the porous support with ILs would enhance the electrostatic interaction, hydrophobic interaction, and hydrogen bond between the porous support and the lipase to efficiently prevent the leakage of lipase from the support (Qin, Zou, Lv, Jin, & Wang, 2016). From this point of view, the IL-modified support is of great potential for the immobilization of lipase since this surface modification can make beneficial improvements in the surface properties for the lipase activity and stability.

More recently, nano-sized porous materials have been exploited as solid matrices in the immobilization of lipase, because the large surface area can greatly improve the lipase loading and the catalytic efficiency of the immobilized lipase (Shuai et al., 2017). However, the drawbacks originated from the nano-biocatalysis are the tedious recycling of the immobilized lipase with nanometer size from the liquid phase and their inevitable loss in the separation process by using filtration or centrifugation, thus resulting in the increased burden of solid–liquid separation for the nanoparticles in particular for the interesterification system of vegetable oils that have a higher viscosity as compared with the conventional reaction system (Netto, Toma, & Andrade, 2013; Xie & Huang, 2018). Therefore, it is of considerable interest to develop an attractive alternative approach to conventional filtration or centrifugation for the biocatalyst recovery.

Among nanostructured materials, magnetic nanoparticles have been identified as a potent catalyst support in catalysis, since they can be readily separated from the reaction mixture especially with minimal loss of the catalyst by applying an external magnetic field (Netto et al., 2013; Xie, Han, & Tai, 2017). However, the unavoidable problems associated with magnetic nanoparticles are their instability over longer periods of time, and in most cases the tendency to aggregate into large clusters due to their magnetic dipole–dipole attractions and their large surface area to volume ratio (Baharfar & Mohajer, 2016). As such, the protection strategies are required to chemically stabilize the naked magnetic nanoparticles. It has been reported that a suitable passive material such as polymer, carbon, and silica can be coated on the magnetic nanoparticles to effectively suppress their aggregations and improve their chemical stabilities (Ranjakhsh, Bordbar, & Abbasi,

2012; Rosenholm, Zhang, Sun, & Gu, 2011; Xie & Wan, 2018; Yang, Li, & Ma, 2012). Accordingly, the integration of mesoporous silica into magnetic nanoparticle seems to be promising and attractive carries for the immobilization of lipase.

In fact, as far as we know there are only a few published literatures on the magnetic immobilized lipase for the organic transformations (Baharfar & Mohajer, 2016; Netto et al., 2013; Shaw, Chen, Ou, & Ho, 2006). As a part of our ongoing project designing efficient and environmentally gentle processes for the modification of vegetable oils (Xie & Zang, 2017), in this contribution, we focused on the synthesis of IL-functionalized core–shell magnetic silica composites used as magnetic carriers for the immobilization of lipase, in which the imidazole-based ILs containing silane coupling groups were covalently grafted on the magnetic silica composites. Thereafter, *Candida rugosa* lipase was then loaded onto the IL-functionalized magnetic composites. The magnetic silica composite and immobilized lipase were characterized in detail by Fourier transform infrared (FT-IR) spectra, transmission electron microscopy (TEM), vibrating-sample magnetometer (VSM), X-ray powder diffraction (XRD), and N₂ adsorption–desorption techniques. By using this biocatalyst, the binary blends of palm stearin (PS) and rice bran oil (RBO) were subjected to the interesterification reactions, and the physicochemical properties of the physical blends and interesterified products were comparatively investigated in terms of FA compositions, TAG profiles, slip melting points (SMPs), and fat crystal microstructures. Furthermore, the reusability of the biocatalyst was also tested in the current research.

The novelty of the present study is associated with the preparation of immobilized lipase with magnetic core–shell structure and its application in the heterogeneous interesterification of PS and RBO. When taking the separation process into consideration, the magnetic feature makes the biocatalyst to be magnetically recyclable with minimal loss, which is a facile and efficient approach as compared with tedious method like filtration or centrifugation.

2. Materials and methods

2.1. Materials

Candida rugosa lipase, tetraethyl orthosilicate (TEOS, ≥98%), cetyltrimethylammonium bromide (CTAB, ≥99%), and 3-chloropropyltriethoxysilane (CPTES, ≥98%) were procured from Sigma-Aldrich. Commercial rice bran oil (RBO) was purchased from a local grocery store (Zhengzhou, China) having the FA composition: 41.2% oleic acid, 33.4% linoleic acid, 1.5% linolenic acid, 21.2% palmitic acid, 1.8% stearic acid, and 0.5% myristic acid. Palm stearin (PS) was provided by Wilmar Biotechnology Research and Development Center (Shanghai, China), and according to GC analysis the FA composition was as follows: 83.9% palmitic acid, 8.9% oleic acid, 4.4% stearic acid, 1.4% linoleic acid, and 1.3% linolenic acid. All other chemicals were analytical or chromatographical grades and used as supplied without further treatment.

2.2. Preparation of IL-functionalized core–shell magnetic composites

Firstly, the Fe₃O₄ magnetite was synthesized by a chemical coprecipitation method according to the previously reported procedure (Shaw et al., 2006). Typically, FeSO₄·7H₂O (3.9 g) and FeCl₃·6H₂O (8.1 g) were dissolved in 150 mL deionized water till the resulting solution became yellowish-orange in color. Thereafter, a certain amount of ammonia solution (25%) was added into the above solution with stirring at room temperature to maintain the pH between 10 and 11. The black suspension, which was produced instantly, was then allowed to continuously stir for 1 h under nitrogen atmosphere. The formed magnetite precipitates were separated by an external permanent magnet, washed repeatedly with deionized water, and finally dried at 60 °C under vacuum for 24 h.

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