Continuous fabrication of calcium sulfate whiskers with adjustable aspect ratio in microdroplets

Yunfei Qi[a], Changfeng Zeng[b], Chongqing Wang[a], Xuebin Ke[c], Lixiong Zhang[a*]

[a] *State Key Laboratory of Materials-Oriented Chemical Engineering and College of Chemistry and Chemical Engineering, Nanjing Tech University, No 5 Xin Mofan Rd., Nanjing, 210009, (PR China)* . E-mail address: lixiongzhang@yahoo.com. Tel.: +86 25 8317 2265; fax: +86 25 8317 2263.

[b] *College of Mechanic and Power Engineering, Nanjing Tech University, No 5 Xin Mofan Rd., Nanjing 210009, PR China*

[c] *School of Engineering, Faculty of Science and Engineering, University of Hull, HU6 7 RX, United Kingdom*

Abstract:

Hemi-hydrate and anhydrous $CaSO_4$ whiskers with adjustable aspect ratio are continuously synthesized by the reactive crystallization of $CaCl_2$ to $K_2S_2O_8$ in microdroplets. The effects of solvent and reactive temperature are examined, with SEM and XRD characterizations. The results indicate that Hemi-hydrate and anhydrous $CaSO_4$ whiskers can be, respectively, obtained in aqueous and N,N-dimethylformamide solutions at 90 °C in 180 s. The addition of ethylene glycol or glycerol can lead to the increase in length and aspect ratio of the whiskers as well as increasing temperature. Thus this preparation technique can continuously synthesize $CaSO_4$ whiskers with two kinds of crystal structures in a short time and adjustable length and aspect ratios.

Keywords: $CaSO_4$, whiskers, crystal growth, crystal structure

1. Introduction

Calcium sulfate whiskers have been widely utilized as reinforcing materials in plastics [1], rubbers [2], paper[3] mills, and grafting materials in bone and tissue regeneration [4-5]. The three forms of calcium sulfate whiskers can be prepared in terms of dihydrate, hemi-hydrate and anhydrous $CaSO_4$, Particularly, the last two forms attract much attention due to their excellent properties in thermal stability, chemical resistance and biocompatibility [6]. hemi-hydrate $CaSO_4$·whiskers can be prepared by dissolution-recrystallization [7-9], reactive crystallization [10-11], or microemulsion [12]. These methods always require long reaction time and/or high reaction temperature, consuming amounts of corrosive materials (crystal modifiers) and expensive surfactants. Anhydrous $CaSO_4$ whiskers are commonly obtained by energy-intensive calcination of dihydrate $CaSO_4$ at 400 °C, or through modifying Ca^{2+} with polymer ligands in organic solvents [13]. Furthermore, all these fabrications are carried out in batch operations, resulting in low production efficiency. It is highly demanded to develop a fast and continuous method to prepare both hemi-hydrate and anhydrous $CaSO_4$ whiskers.

Herein, we develop a facile and continuous technique to synthesize hemi-hydrate and anhydrous $CaSO_4$ whiskers with adjustable aspect ratio at low temperatures within several minutes. the morphology and the aspect ratio of the whiskers can be adjusted by Changing the solvent or temperature.

2. Experimental

Continuous fabrication of calcium sulfate whiskers is conducted in a home-made coaxial microfluidic device. two micro-needles (Φ0.34 mm in diameter) are assembled into a PTFE tube (Φ1mm x 400 mm) which is immersed in a water bath [14]. Liquid paraffin is used as continuous phase, and $CaCl_2$ and potassium persulfate ($K_2S_2O_8$,KPS) in different solvents as dispersed phase, such as N, N-dimethyformamide (DMF), ethylene glycol (EG), and glycerol (GL). Typically, 0.9 M $CaCl_2$ aqueous solution and 0.45 M KPS aqueous solution are prepared. The $CaCl_2$ and KPS solutions are pumped into two needles at a flow rate of 0.1 and 2 ml/h, respectively. Then the generated aqueous droplets are transported by continuous phase at a temperature of 90 °C and retention time of 180 s. The effluents are collected in a beaker precharged with petroleum ether, and the product is obtained after filtrating, washing with ethanol, and drying.

3. Result and discussion

The continuous fabrication of calcium sulfate whiskers is conducted by heating $CaCl_2$ and KPS microdroplets. The KPS is decomposed to release SO_4^{2-}, which subsequently react with Ca^{2+} to form calcium sulfate. the preparation is firstly carried out using aqueous solutions of $CaCl_2$ and KPS at 90 ºC. The SEM picture of the resultant product (Fig 1a) reveals the formation of whiskers with the length of 1.62-10.33 μm and the width of 0.13-2.26 μm. The XRD pattern (Fig 2a) verifies the formation of hemi-hydrate $CaSO_4$ (JCPDS No.41-0224) with feature peaks at ???. However, the aspect ratio is relative low of only 2.5-18.7. we replace water with EG in the formation of KPS solution, as they can promote the growth of $CaSO_4{\cdot}0.5H_2O$ whiskers along the c axis [15]. The obtained product exhibits a XRD pattern in consistent with the standard peaks for $CaSO_4{\cdot}0.5H_2O$ (Fig 2a). The fibril-like morphology is shown in the SEM picture (Fig 1b). The length is 34.1-62.4 μm and the width is 0.26-0.67 μm, with the aspect ratio up to 49-127. Furthermor, we use GL to replace EG [16]. The similar results are obtained and the whisker-like crystals have The length of 27.2-56.7 μm and the width of 0.31-0.84 μm. the aspect ratio is 43-109, a bit less than that using EG. These results suggest that $CaSO_4 \cdot 0.5H_2O$ whiskers can be continuously prepared, and their aspect ratio can be adjusted.

As above the preparations use the aqueous solutions of $CaCl_2$ $CaSO_4 \cdot 0.5H_2O$ whiskers are obtained. we replace water with DMF in the $CaCl_2$ solutions to prepare anhydrous $CaSO_4$ whiskers, which are more stable than $CaSO_4 \cdot 0.5H_2O$ whiskers [6]. The SEM observation of the resulting product (Fig 1d) indicates that they exhibit rod-like morphology, with a length of 16.4-63.2 μm, a width of 1.2-6.2 μm and the aspect ratio of 13-32. The XRD pattern (Fig 2b) verifies the formation of anhydrous $CaSO_4$ (JCPDS No.43-0606), corresponding to the feature peaks at ???. We also substitute DMF with EG and GL in the KPS solution to prepare anhydrous $CaSO_4$ whiskers. The results indicate that the product with EG has a length of 24.3-59.5 μm, a width of 0.23-0.76 μm, and aspect ratio of 48-121 μm (Fig 1-e). In the case of GL in the KPS solution the length is 28.2-54.4 μm, width of 0.21-0.89 μm, and aspect ratio of 41-106 (Fig 1f).

In both aqueous and DMF solutions of $CaCl_2$, EG in the KPS solution can result in the formation of whiskers with longer aspect ratios than GL. This can be ascribed to more hydroxyl groups in GL, which can restrain the growth of (001) facets. As the amount of hydroxyl groups is more than that to saturated adsorb on the (200), (400), and (220) facets, the extra hydroxyl groups may adsorb on the (001) facets of whiskers [15-16]. Besides, the viscosity of GL is higher than EG at the same temperature, which may suppress the interaction between hydroxyl group to Ca^{2+} and Ca^{2+} to SO_4^{2-}.

To examine the effect of temperature, we conduct the preparation using both DMF and aqueous solutions with GL at 50 °C and 70 °C, and compare the results with those prepared at 90 °C as shown above (Table 1). It is apparent that the length and aspect ratio of the whiskers obtained from both solutions increase, with the increasing temperature while the width shows a reverse tendency. This can be explained by The fast decomposition of KPS at higher temperatures results in the increasing concentration of SO_4^{2-} in the reaction system. A high concentration leads to a high saturation degree, favoring the nucleation and growth of crystals. As the growth of the (200), (400), and (220) facets are inhibited by adsorption of GL, the growth in (001) facet is accelerated, thus leading to the increasing length and decreasing width [16].

Table 1 The calcium sulfate whiskers prepared at different temperatures

T/°C	Aqueous solution			DMF solution		
	Length(μm)	Width(μm)	Aspect ratio	Length(μm)	Width(μm)	Aspect ratio
50	17.5-45.6	0.55-2.32	18-37	15.4-43.7	0.94-3.16	12-29
70	24.5-50.2	0.47-1.27	29-64	19.6-49.6	0.78-1.86	26-57
90	27.2-56.7	0.31-0.84	43-109	28.2-54.4	0.21-0.89	41-106

4. Conclusion

We develop a continuous microfluidic technique for the preparation of calcium sulfate whiskers. Decomposition of KPS at high temperatures facilitate the releases of SO_4^{2-}, which reacts with Ca^{2+} to form $CaSO_4$. $CaSO_4 \cdot 0.5H_2O$ and anhydrous $CaSO_4$ whiskers can be, respectively, prepared in aqueous and DMF solutions. The additions of EG and GL can significantly increase the aspect ratio of the resulting whiskers as well as the increasing temperature. The preparation time is less than 3 min, much shorter than those needed in batch operations. Such continuous process can remarkably enhance productivity and facile regulate the lengths and aspect ratios of $CaSO_4$ whiskers

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 21476114), Natural Science Key Project of the Jiangsu Higher Education Institutions

(No.12KJA530002), and Priority Academic Program Development of Jiangsu Higher Education Institutions.

Reference

[1] H.G. Wang, B. Mu, J.F. Ren, L.Q. Jian, J.Y. Zhang, S.R. Yang, Mechanical and tribological behaviors of PA66/PVDF blends filled with calcium sulphate whiskers, Polym. Compos. 30 (2009) 1326-1332.

[2] J.C. Wang, X.C. Pan, Y. Xue, S. J. Cang, Studies on the application properties of calcium sulfate whisker in silicone rubber composites, J. Elastomers. Plast. 44 (2011) 55–66.

[3] X. Feng, Y. Zhang, G.L. Wang, M. Miao, L.Y. Shi, Dual-surface modification of calcium sulfate whisker with sodium hexametaphosphate/silica and use as new water-resistant reinforcing fillers in papermaking, Powder. Technol. 271 (2015) 1–6.

[4] J.V.D. Stok, E.M.M.V. Lieshout, Y.E. Massoudi, G.H.V. Kralingen, P. Patka, Bone substitutes in the Netherlands-a systematic literature review, Acta. Biomater. 7 (2011) 739-750.

[5] M.V. Thomas, D.A. Puleo, Calcium sulfate: properties and clinical applications, J. Biomed. Mater. Res. B. 88 (2009) 597-610.

[6] D. Freyer, W. Voigt, Crystallization and phase stability of $CaSO_4$ and $CaSO_4$-based salts, Monatsh. Chem. 134 (2003) 693-719.

[7] X. Wang, L.S Yang, X.F Zhu, J.K. Yang, Preparation of calcium sulfate whiskers from FGD gypsum via hydrothermal crystallization in the H_2SO_4-NaCl-H_2O system, Particuology. 17 (2014) 42-48.

[8] S.C. Hou, J. Wang, X.X. Wang, H.Y. Chen, L. Xiang, Effect of Mg^{2+} on Hydrothermal Formation of α-$CaSO_4\cdot0.5\ H_2O$ Whiskers with High Aspect Ratios, Langmuir. 30 (2014)

9804-9810.

[9] L. Li, Y.J. Zhu, M.G. Ma, Microwave-assisted preparation of calcium sulfate nanowires, Mater. Lett. 62 (2008) 4552-4554.

[10] X.F Song, L.N. Zhang, J.C. Zhao, Y.X. Xu, Z. Sun, P. Li, J.G. Yu, Preparation of calcium sulfate whiskers using waste calcium chloride by reactive crystallization, Cryst. Res. Technol. 46 (2011) 166-172.

[11] X.L. Mao, X.F. Song, G.M. Lu, Y.Z. Sun, Y.X. Xu, J.G. Yu, Effects of metal ions on crystal morphology and size of calcium sulfate whiskers in aqueous HCl solutions, Ind. Eng. Chem. Res. 53 (2014) 17625-17635.

[12] B. Kong, B.H. Guan, M.Z. Yates, Z.B. Wu, Control of α-calcium sulfate hemihydrate morphology using reverse microemulsions, Langmuir. 28 (2012) 14137-14142.

[13] X.Y. Song, S.X. Sun, W.L. Fan, H.Y. Yu, Preparation of different morphologies of calcium sulfate in organic media, J. Mater. Chem. 13 (2003) 1817-1821.

[14] L. Yu, Y.C. Pan, C.Q. Wang, L.X. Zhang, A two-phase segmented microfluidic technique for one-step continuous versatile preparation of zeolites, Chem. Eng. J. 219 (2013) 78-85.

[15] W.P. Zhao, Y.M. Wu, J. Xu, C.H. Gao, Effect of ethylene glycol on hydrothermal formation of calcium sulfate hemihydrate whiskers with high aspect ratios, RSC. Adv. 5 (2015) 50544-50548.

[16] H. He, F.Q. Dong, P. He, L.H. Xu, Effect of glycerol on the preparation of phosphogypsum-based $CaSO_4 \cdot 0.5H_2O$ whiskers, J. Mater. Sci. 49 (2014) 1957-1963.

Figure captions:

Fig. 1 SEM images of the samples prepared in different solutions at 90 ºC. $CaCl_2$ aqueous solution and KPS aqueous solution (a), KPS EG solution (b) and KPS GL solution (c); $CaCl_2$ and KPS DMF solutions (d), KPS EG solution (e) and GL solution (f).

Fig. 2 XRD patterns of the whiskers prepared in different solutions at 90 ºC. (a) aqueous solution; (b) DMF solution.

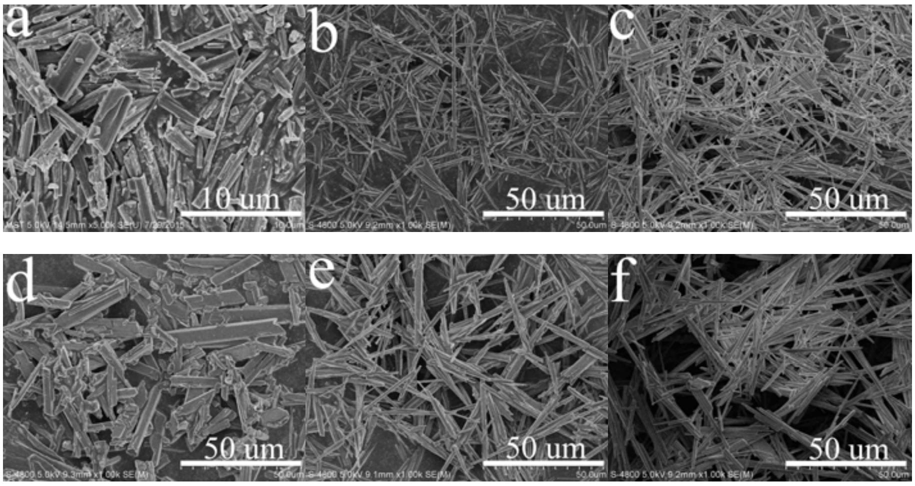

Fig. 1 SEM images of the samples prepared in different solutions at 90 ºC. $CaCl_2$ aqueous solution and KPS aqueous solution (a), KPS EG solution (b) and KPS GL solution (c); $CaCl_2$ and KPS DMF solutions (d), KPS EG solution (e) and GL solution (f).

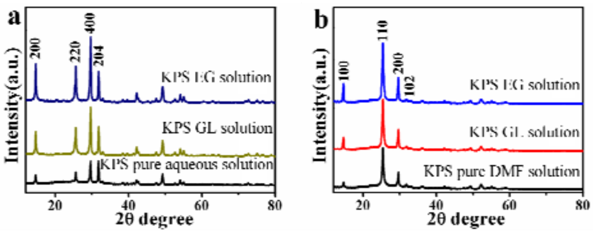

Fig. 2 XRD patterns of the whiskers prepared in different solutions at 90 oC. (a) aqueous solution; (b) DMF solution.