Controllable synthesis of high aspect ratio $Mg_2B_2O_5$ nanowires and their applications in reinforced polyhydroxyalkanoate composites*

Mo Zhao-Jun(莫兆军), Chen Jin-Peng(陈金鹏), Lin Jing(林 靖)†,
Fan Ying(范 英), Liang Chun-Yong(梁春永), Wang Hong-Shui(王洪水),
Xu Xue-Wen(徐学文), Hu Long(胡 龙), and Tang Cheng-Chun(唐成春)‡

School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, *China*

(Received 7 October 2013; revised manuscript received 10 December 2013; published online 25 March 2014)

Highly pure magnesium borate ($Mg_2B_2O_5$) nanowires with an average diameter of $\sim$ 30 nm, an average length of $\sim$ 15 μm, and a high aspect ratio of $\sim$ 500 have been synthesized on a large scale via a two-step method. $MgBO_2(OH)$ nanowires with high aspect ratios were first prepared via a PVP-assisted hydrothermal technique. Using these nanowires as precursors, single crystalline $Mg_2B_2O_5$ nanowires were synthesized by post-annealing treatment at a relatively low temperature of 700 °C. The important effect of the $MgBO_2(OH)$–$Mg_2B_2O_5$ conversion process on the morphology of the $Mg_2B_2O_5$ nanowires was investigated and it was indicated that the recrystallization process plays an important role in the protection of the one-dimensional (1D) nanostructure. Moreover, the rigidity and the toughness of the $Mg_2B_2O_5$ nanowire-reinforced PHA composites were tremendously improved compared to those of the pure PHA. Our results demonstrate the effectiveness of $Mg_2B_2O_5$ nanowires for reinforcement applications in polymer composites.

Keywords: nanostructure, recrystallization, reinforcement

PACS: 62.23.St, 81.10.Jt, 43.38.Tj **DOI:** 10.1088/1674-1056/23/5/056201

1. Introduction

Metal borate is one of the most important technical ceramics owing to its interesting properties, such as high heat resistance and corrosion resistance, superb mechanical strength, superb insulation, and a high coefficient of elasticity.[1] Among the various kinds of metal borates, the magnesium borate ($Mg_2B_2O_5$) whisker has been considered to have promise as a reinforcing component in composite material applications due to its excellent mechanical properties, attractive thermal properties, thermo-luminescent properties,[2] and good anti-wear behavior.[3] In recent years, there has been a great deal of research in the use of $Mg_2B_2O_5$ whiskers to reinforce Mg and Al matrix composites,[4] which has had considerable success. It should be noted that the excellent mechanical properties of the $Mg_2B_2O_5$ whiskers also imply their promise as a reinforcing additive for polymers. Polyhydroxyalkanoate (PHA) is a class of natural polyesters and is currently under extensive investigation. This kind of polyester can be biologically synthesized from bio-renewable feedstocks and is generally biodegradable and biocompatible.[5] However, the brittle nature of the PHA polymers has hindered their development in practical applications. Reinforcing PHA polymers by the incorporation of $Mg_2B_2O_5$ nanowires provides the possibility to obtain composite materials with high mechanical strength. However, the related study has not yet been initiated, and this presents a challenge.

Since reducing the size of whiskers into a nanometer scale can greatly enhance their toughness and strength,[6–8] one-dimensional (1D) $Mg_2B_2O_5$ nanostructures are considered to be a better candidate to reinforce composites compared with their micron-sized counterparts. It should be noted that the novel properties of the 1D nanostructures greatly depend on their morphologies and aspect ratios (length versus diameter). Nanowires with high aspect ratios could be more beneficial to strengthen the traditional materials. Therefore, the controlled synthesis of high aspect-ratio $Mg_2B_2O_5$ nanostructures has become an important focus for their development in composite applications. So far, there has been great progress in the synthesis of 1D $Mg_2B_2O_5$ nanostructures[9–12] based on various synthetic routes, such as high-temperature sintering and chemical vapor deposition (CVD). For example, using $MgCl_2{\cdot}6H_2O$ and $NaBH_4$ as starting materials, Li *et al.*[13] synthesized single-crystal $Mg_2B_2O_5$ nanorods with diameters of 200–400 nm and lengths up to 5 μm by a two-step process involving a mechanochemical technique and sintering. Yi *et al.*[14] synthesized large quantities of single crystalline $Mg_2B_2O_5$ nanowires, with typical diameters of 120–180 nm and lengths of 0.2 mm, through direct heating of a mixed tablet of $Mg(BO_2)_2$ and graphite in vacuum at 1200 °C for 1 h. Compared with high-temperature sintering or CVD, the

*Project supported by the National Natural Science Foundation of China (Grant No. 10974041), the Research Fund for the Dectoral Program of Higher Education, China (Grant No. 20091317110005), the Key Projects of Chinese Ministry of Education (Grant No. 209011), and the Natural Science Foundation of Hebei Province, China (Grant No. 2010000084).

†Corresponding author. E-mail: Dr.linjing@gmail.com

‡Corresponding author. E-mail: tangcc@hebut.edu.cn

© 2014 Chinese Physical Society and IOP Publishing Ltd

hydrothermal synthesis has shown some distinct advantages for preparing uniform nanocrystals with high crystallinity and high purity, such as the moderate experimental conditions and the easy control of the process parameters.[15,16] Previous studies have indicated that 1D $Mg_2B_2O_5$ nanostructures can be prepared at a relatively low temperature based on the post-annealing of hydrothermally synthesized $MgBO_2(OH)$ nanostructures.[17,18] Zhu *et al.*[19,20] reported the preparation of $Mg_2B_2O_5$ nanowhiskers with diameters of 15.0–45.0 nm and lengths of 0.2–2.0 μm by a low-temperature annealing treatment at 650–700 °C using hydrothermally synthesized $MgBO_2(OH)$ nanowires as precursors. However, breakage was unavoidable during the thermal conversion from $MgBO_2(OH)$ to $Mg_2B_2O_5$ nanowires. The authors[21] also tried to directly synthesize $Mg_2B_2O_5$ by co-precipitation and calcination at 800–900 °C for 2 h. However, they failed in the synthesis of $Mg_2B_2O_5$ nanowires. To date, developing a synthetic strategy to prepare high aspect-ratio $Mg_2B_2O_5$ nanowires at a low temperature is still a major challenge.

In this paper, we report pioneering large-scale preparation of uniform $Mg_2B_2O_5$ nanowires with an aspect ratio as high as ~ 500 based on a two-step method. $MgBO_2(OH)$ nanowires with high aspect ratios were first prepared via a polyvinylpyrrolidone (PVP)-assisted hydrothermal technique. Then, by using the as-prepared $MgBO_2(OH)$ nanowires as precursors, single crystalline $Mg_2B_2O_5$ nanowires were synthesized by post-annealing treatment at a relatively low temperature of 700 °C. A detailed thermal conversion analysis was performed that gave vital clues to understand the recrystallization process from $MgBO_2(OH)$ to $Mg_2B_2O_5$. The slower heating rate was critical to obtain high aspect ratio 1D $Mg_2B_2O_5$ nanowires in this process. Then, for the first time, the as-prepared $Mg_2B_2O_5$ nanowires were used as an additive in PHA polymers to form composites. A remarkable increase of the rigidity and toughness of the composite has been obtained by the addition of $Mg_2B_2O_5$ nanowires into PHA. Our results have demonstrated the effectiveness of $Mg_2B_2O_5$ nanowires for reinforcement applications in polymer composites.

2. Experimental details

Synthesis of $MgBO_2(OH)$ nanowires The starting materials of $MgCl_2$, H_3BO_3, NH_4OH, and PVP were commercial grade and used without further purification. $MgCl_2$ (1.904 g) and H_3BO_3 (1.855 g) were resolved in deionized water (25 ml), and PVP (0–1.5 g) was added into the solution and stirred for 1 h. Then, NH_4OH (10 ml) was carefully sprayed into the solution and stirred for another 1 h to obtain a slurry as the precursor. Subsequently, the slurry was put into a Teflon-lined stainless steel autoclave. The slurry (precursor) was heated at 220 °C for 24 h and cooled down to room temperature. Finally the products were filtered and washed several times with deionized water and dried at 120 °C for 12 h.

Synthesis of $Mg_2B_2O_5$ nanowires The as-prepared $MgBO_2(OH)$ nanowires were placed in an alumina crucible and used as the initial reaction constituent. The alumina crucible was situated in an alumina tube and first heated at 360 °C with different heating rates (1–10 °C·min^{-1}) for 4 h; it was then heated (1–10 °C·min^{-1}) to 600 °C for another 4 h; finally, it was heated (1–10 °C·min^{-1}) to 700 °C for another 4 h to recrystallize. All the thermal conversions were accomplished in air using a traditional resistance heating furnace. The resultant samples were then collected for characterization.

Synthesis of $Mg_2B_2O_5$ anowire-reinforced PHA First 2.4 mg $Mg_2B_2O_5$ nanowires were dispersed into 20 ml chloroform by stirring and ultrasound treatment for 1 h, respectively. Then, 1.2 g PHA was put into the mixed solution and the stirring was continued until a translucent and homogeneous colloidal solution was obtained at 50 °C. Finally, films with a thickness of ~ 0.1 mm and diameter of ~ 10 cm were cast at room temperature for several hours.

Characterization The structure and the morphology of the samples were identified by X-ray powder diffraction (XRD, BRUKER D8 FOCUS), a field emission scanning electron microscopy (SEM, HITACHI S-4800), and a high resolution transmission electron microscopy (HRTEM, JEM-2010). The thermal decomposition behavior of the sample was detected by differential thermal analysis (TG-DTA, SDT22960, TA Instruments, USA), which was carried out in dynamic air from room temperature to 900 °C at a heating rate 10 °C·min^{-1}. For the mechanical measurement, the as-prepared films were stretched on a Micro Bionix equipped with a 5 N load cell (MTS Systems Corporation) at a strain rate of 30 mm·min^{-1}. Test Star IIV 4.0 (MTS Systems Corporation) was used as the data collection and equipment control software. The test samples were trimmed to 4 mm wide and 25 mm long and the casting resulted in films that were approximately 0.1 mm thick. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Morphology and structure of $MgBO_2(OH)$ nanowires

Figure 1(a) shows the XRD pattern of the hydrothermally synthesized products. All the diffraction peaks can be indexed to a monoclinic $MgBO_2(OH)$ with lattice parameters of $a = 1.2588$, $b = 1.0400$, $c = 0.3125$ nm, and $\beta = 95.88$ °C. This result is in good accordance with those reported for the bulk crystal (PDF No. 33-0859). The diffraction peaks suggest that the samples were well crystallized. No XRD peaks arising from impurities were detected, indicating the high purity of the product. The low-magnification SEM image (Fig. 1(b)) shows

a large yield of highly flexible nanowires with lengths of several tens of micrometers. The enlarged SEM image (Fig. 1(c)) indicates that the nanowires have diameters of ∼ 20–60 nm. The aspect ratio of the nanowires can be determined to be as high as ∼ 500. Therefore, we can conclude that high-aspect ratio $MgBO_2(OH)$ nanowires have been fabricated with high yield and high purity.

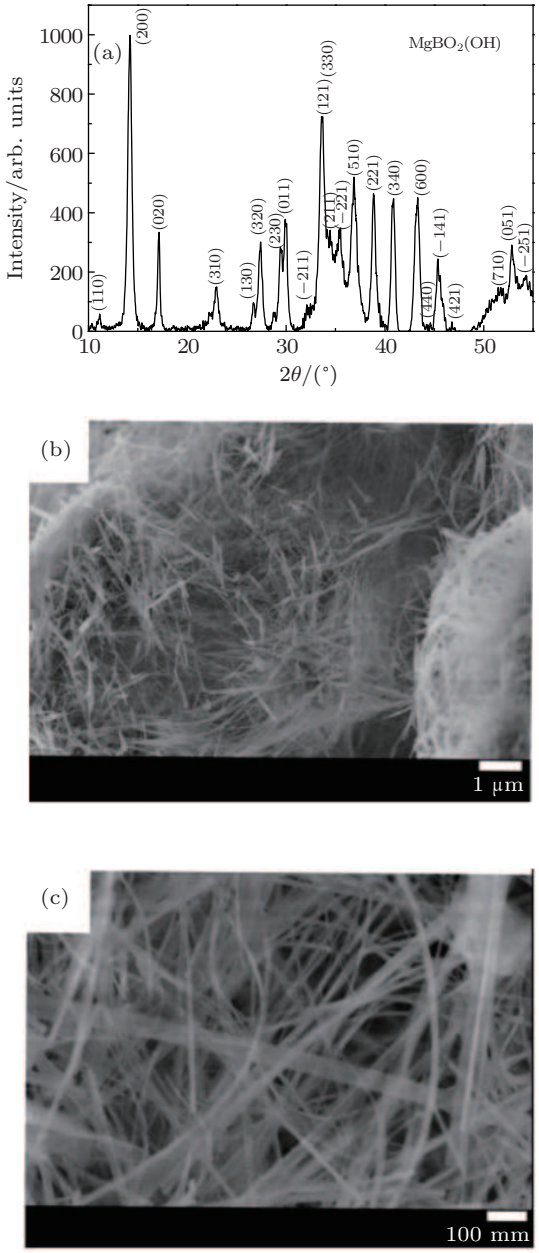


Fig. 1. (a) XRD pattern of the final products. (b) Low-magnification SEM image of the as-prepared nanowires. (c) Enlarged SEM image of the $MgBO_2(OH)$ nanowires.

PVP has been considered to be an important surfactant for the hydrothermal synthesis of 1D nanostructures.[22] Due to its strong ability forming hydrogen bonding and complex, PVP is favorable for promoting 1D preferential growth and increasing the aspect ratio of 1D nanostructures. The effect of PVP on the aspect ratio of the $MgBO_2(OH)$ nanowires is studied in Fig. 2. A considerable dependence of the aspect ratio on the content of PVP is exhibited. Very short nanorods with an average diameter of ∼ 45 nm and an average length of ∼ 800 nm were obtained when PVP was not added during the synthesis process (Fig. 2(a)). As the PVP content increased to 0.1 g, the average length of the nanorods increased (Fig. 2(b)). When the PVP content was increased to 0.5 g, tremendously longer $MgBO_2(OH)$ nanowires with lengths of several tens of micrometers and an average diameter of ∼ 30 nm were obtained (Fig. 2(c)). However, the PVP addition did not help to increase the aspect ratio of the nanowires further. Figures 2(d) and 2(e) show the SEM images of the $MgBO_2(OH)$ nanowires with PVP contents of 1.0 g and 1.5 g, respectively. Figure 2(f) shows the average aspect ratio as a function of the PVP content. The ratio rapidly increases as the PVP content increases from 0 g to 0.5 g, and it then decreases as the PVP content continuously increases from 0.5 g to 1.5 g. Therefore, we can conclude that the usage of PVP is a key factor for the formation of $MgBO_2(OH)$ nanowires with high aspect ratio, and the optimal PVP content is 0.5 g.

Figure 3(a) shows the TG-DTG curves of the $MgBO_2(OH)$ nanowires, which were hydrothermally synthesized under the optimal synthetic conditions (the morphology of the nanowires is shown in Fig. 2(c)). The results clearly show that the sample lost weight at a comparatively slow rate at temperatures below 360 °C, and at a fast rate in the temperature range of 360–600 °C. When the heating temperature was increased above 600 °C, the sample weight remained almost constant, with very little variation. The sample weight loss during the heating process is related to the elimination of physically absorbed water and structural water, respectively. The weight loss between 360 °C and 600 °C was 10.67%, which is quite similar to the theoretical weight loss (10.7%) for the conversion of $MgBO_2(OH)$ to $Mg_2B_2O_5$. It also indicates that the dehydration process was basically completed at 600 °C. The conversion can be expressed as

$$2MgBO_2(OH)\ (s) \rightarrow Mg_2B_2O_5\ (s) + H_2O\ (g). \qquad (1)$$

The decomposition temperature was lower than that of natural $MgBO_2(OH)$. The smaller particle size may result in the reduction of the decomposition temperature. The DTA curve shows a remarkable endothermic peak at ∼ 575 °C and a sharp exothermic peak at ∼ 664 °C. The endothermic peak corresponds to the conversion of $MgBO_2(OH)$ to $Mg_2B_2O_5$, and the sharp exothermic peak at 664 °C corresponds to the recrystallization of $Mg_2B_2O_5$. The results indicate that most of the structural water was eliminated at ∼ 600 °C, whereas a higher temperature was still required to complete the recrystallization of the nanowires.

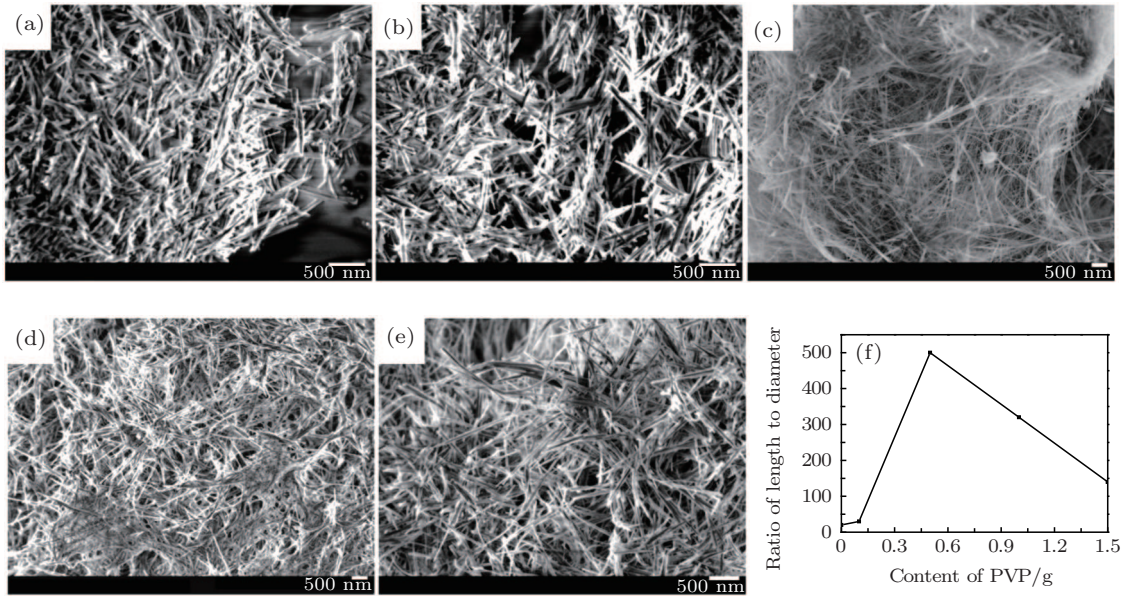


Fig. 2. (color online) (a)–(e) SEM images of $MgBO_2(OH)$ nanowires synthesized with different contents of PVP: (a) 0 g, (b) 0.1 g, (c) 0.5 g, (d) 1.0 g, (e) 1.5 g. (f) Aspect ratio of $MgBO_2(OH)$ nanowires as a function of PVP content.

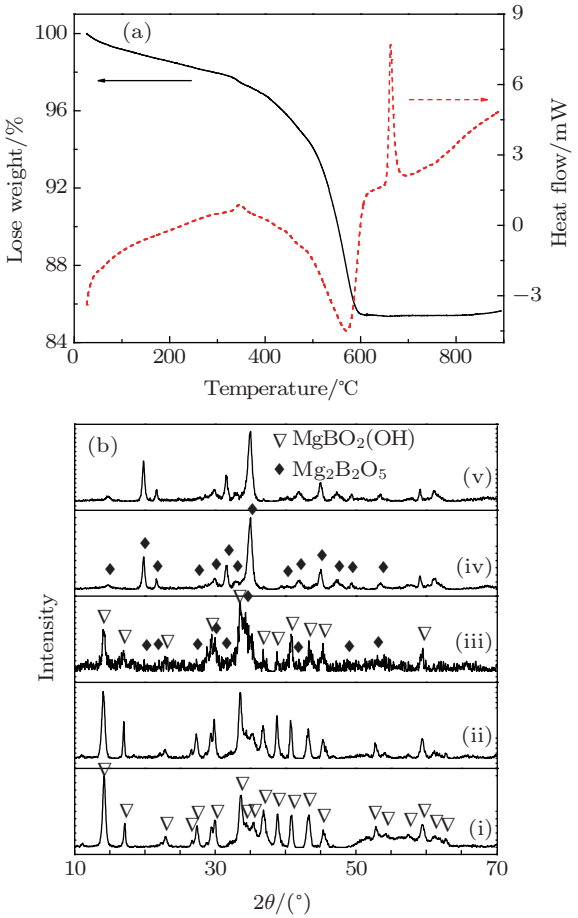


Fig. 3. (color online) (a) TG–DTG curves of the $MgBO_2(OH)$ nanowires; (b) XRD patterns of the products calcined at different temperatures: (i) precursor, (ii) 360 °C, (iii) 600 °C, (iv) 700 °C, (v) 850 °C.

Figure 3(b) shows the XRD patterns of the products calcined at different temperatures. When the $MgBO_2(OH)$ nanowires were calcined at 360 °C (curve ii), there was almost no change in composition compared with the precursor (curve i). The samples only lost physically absorbed water. Although most of the structural water was eliminated when the temperature was increased to 600 °C, the sample was still mainly $MgBO_2(OH)$ (curve iii). A higher temperature was required to complete the recrystallization of $Mg_2B_2O_5$. When the temperature was increased to 700 °C, the sample was well crystallized. All diffraction peaks could be indexed to a triclinic $Mg_2B_2O_5$ with lattice parameters of $a = 0.6160$, $b = 0.9210$, $c = 0.3109$ nm and $\alpha = 90.47°$, $\beta = 92.12°$, $\gamma = 104.4°$. These results are quite consistent with those reported in PDF No. 15-0537. No peak attributable to possible impurities was observed, which indicates that only elemental $Mg_2B_2O_5$ with high purity was obtained. After further increasing the calcined temperature to 850 °C none of the diffraction peaks had changed compared with the diffraction peaks of 700 °C. These results indicate that the recrystallization of $Mg_2B_2O_5$ has been completed at 700 °C. Therefore, the conversion temperature from $MgBO_2(OH)$ nanowires to $Mg_2B_2O_5$ nanowires should be controlled at about 700 °C to ensure the formation of pure phase $Mg_2B_2O_5$ nanowires.

The heating rate during the thermal conversion from $MgBO_2(OH)$ to $Mg_2B_2O_5$ plays an important role in the final morphology of the $Mg_2B_2O_5$ nanowires. Figure 4 shows the typical SEM images of the $Mg_2B_2O_5$ nanowires treated under different heating conditions. Figure 4(a) shows the morphologies of the products formed at 360 °C, with different heating rates from 1 °C·min^{-1} to 10 °C·min^{-1}. With the increase of the heating rate, the phenomenon of nanowire breaking did not occur, because the precursor just lost the physically absorbed water. Generally speaking, missing the structural water would lead to an imbalance of the molecular structure and produce an

inner stress that leads to a serious fracture. However, when the heating rate was increased, the original morphology was still not destroyed at 600 °C, as can be seen in Fig. 4(b). One possible reason for this is that the inner stress occurring during the heating process at 600 °C was not strong enough and could be quickly released from the thin nanowires. Figure 4(c) shows the effect of recrystallization at 700 °C on the morphology of the products. The molecular structure was recomposed and a stronger stress was generated in this process. When the heating rate was 10 °C·min^{-1}, the crystal structure was quickly recomposed and there was not enough time to release the rapidly generated inner stress. Therefore, a serious nanowire fracture occurred. A slower heating rate is favorable to keep the morphology of high aspect-ratio nanowires since there is enough time to ensure the dispersion of the inner stress during the heating process. Therefore, we can conclude that the heating rate is important in order to protect the aspect ratio of $Mg_2B_2O_5$ nanowires in recrystallization. The recrystallization process is critical to obtain high aspect-ratio 1D $Mg_2B_2O_5$ nanowires and a slower heating rate is favorable to protect the previous morphology in the recrystallization process.

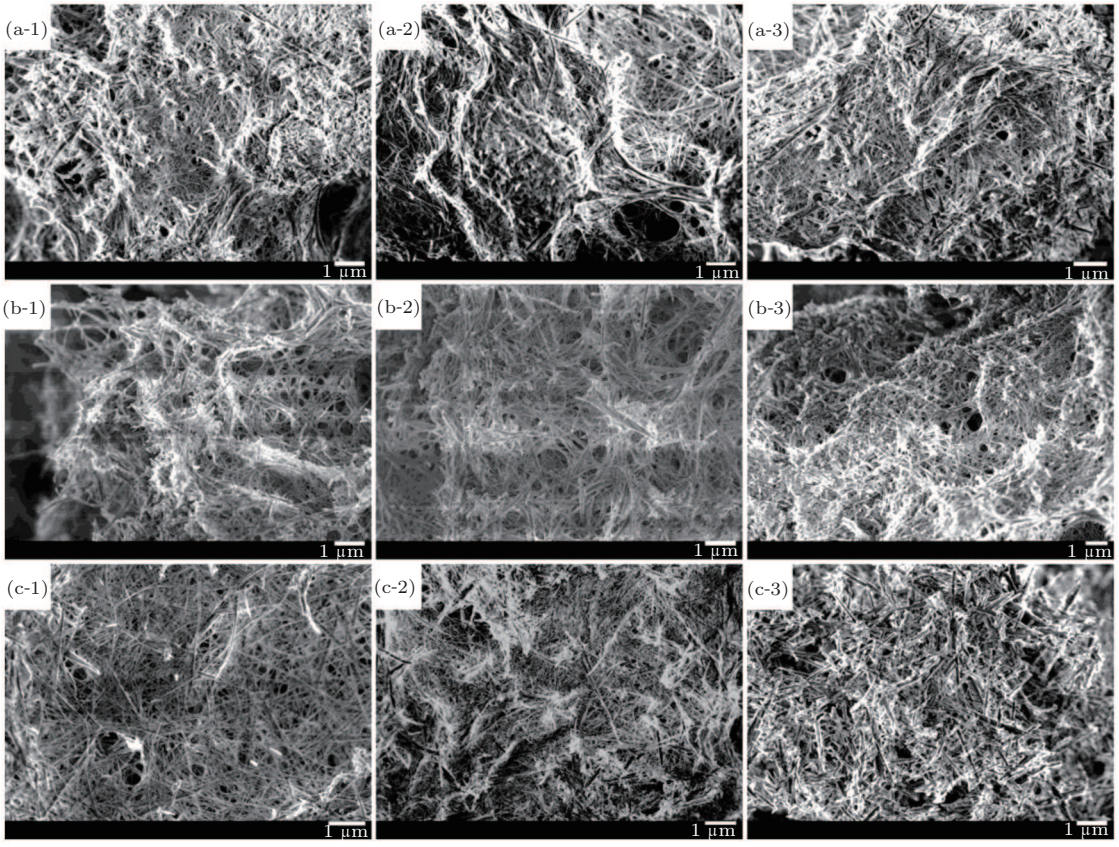


Fig. 4. SEM images of the products calcined at different temperatures and heating rates: (a-1) 360 °C, 1 °C·min^{-1}; (a-2) 360 °C, 5 °C·min^{-1}; (a-3) 360 °C, 10 °C·min^{-1}; (b-1) 600 °C, 1 °C·min^{-1}; (b-2) 600 °C, 5 °C·min^{-1}; (b-3) 600 °C, 10 °C·min^{-1}; (c-1) 700 °C, 1 °C·min^{-1}; (c-2) 700 °C, 5 °C·min^{-1}; (c-3) 700 °C, 10 °C·min^{-1}.

The above work has shown that a slow heating rate is favorable for the formation of $Mg_2B_2O_5$ nanowires with high aspect ratio in the recrystallization process. Figure 5 shows typical SEM and TEM images of nanowires synthesized under optimal synthetic conditions. Uniform $Mg_2B_2O_5$ nanowires with an average diameter of $\sim$ 30 nm can be observed in Fig. 5(a). Figure 5(b) exhibits the typical morphology of the $Mg_2B_2O_5$ nanowires, establishing a diameter distribution which is in agreement with the SEM observation. The explicit lattice fringes along the longitudinal direction of the nanowires were detected with the inter-planar spacing (0.590 nm) in Fig. 5(c), which is quite consistent with that (0.596 nm) of the (100) planes for triclinic $Mg_2B_2O_5$, indicating the preferential growth of the nanowires along the *c* axis.

The formation of $Mg_2B_2O_5$ nanowires involves a process of co-precipitation, hydrothermal, and dehydration recrystallization, as depicted in Fig. 6. Amorphous irregular $MgB_3O_3(OH)_5{\cdot}5H_2O$ and $Mg_7B_4O_{13}{\cdot}7H_2O$ nanoflakes were first formed during the co-precipitation process at room temperature. These nanoflakes were then gradually dissolved as the hydrothermal temperature was continuously increased to 220 °C. At the same time, crystalline 1D $MgBO_2(OH)$ nanostructures began to form under the assistance of PVP. The PVP played an important role in this process. It has been reported

that PVP possesses an excellent adsorption ability and can selectively adsorb on special facets of a crystal by physical adsorption or chemical adsorption.[23] Herein, PVP could selectively adsorb on special facets of $MgBO_2(OH)$ and confine the growth of these directions. So, $MgBO_2(OH)$ nuclei grow along a contained direction. Under continuous growth, 1D $MgBO_2(OH)$ nanowires were formed. $Mg_2B_2O_5$ nanowires were synthesized based on the $MgBO_2(OH)$ nanowires by dehydration and recrystallization at 700 °C. In this process, the physically absorbed water and the structural water were eliminated at 360 °C and 600 °C, respectively. The heating rate was not relevant with the morphology in the dehydration process. However, the heating rate played an important role in the protection of 1D nanostructure in the recrystallization process at 700 °C. A slow heating rate (1 °C·min^{-1}) is favorable for protecting the 1D nanostructure.

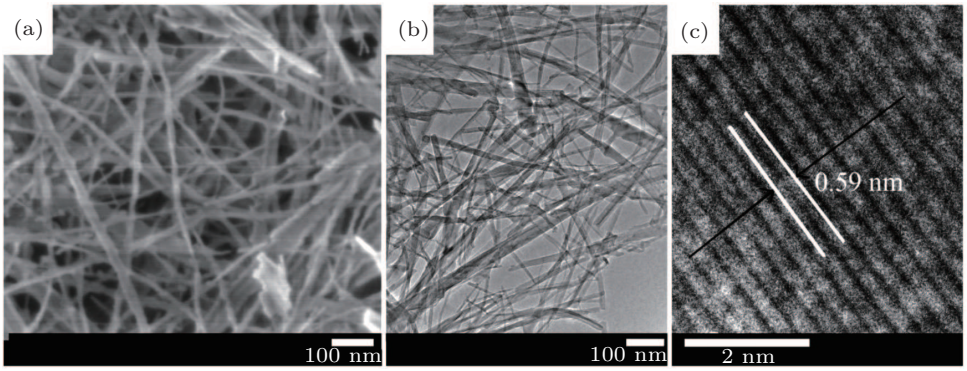


Fig. 5. (a) High-magnification SEM image the $Mg_2B_2O_5$ nanowires calcined at 700 °C with a heating rate of 1 °C/min; (b) low-magnification TEM image of the nanowires; (c) high-magnification TEM image of the nanowires.

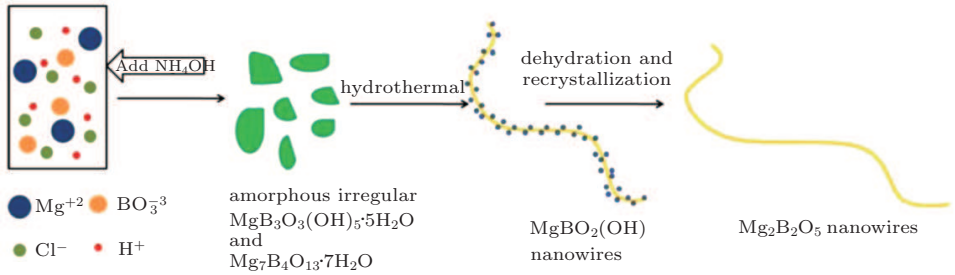


Fig. 6. (color online) Formation mechanism of the $Mg_2B_2O_5$ nanowires.

3.2. $Mg_2B_2O_5$ nanowire-reinforced PHA composites

In order to obtain PHA polymers with high mechanical strength, the as-prepared $Mg_2B_2O_5$ nanowires were used as an additive in PHA polymers to form composites. We then studied the mechanical properties of the composites with various contents of $Mg_2B_2O_5$. Figure 7 illustrates representative stress-strain curves for the polymer samples. The elongation at failure is a measurement of toughness and reflects the total deformation that a polymer can withstand before fracture. The Young's modulus is a measure of stiffness that considers the slope of the stress response to deformation at very low strains. The ultimate tensile strength is a measure of the maximum strength of the material prior to the onset of plastic deformation. This value is obtained from the maximum of the initial peak in the stress versus strain diagram. Excised samples from the films were subjected to a strain applied at a steady rate in a pure extensional direction. The resulting force response was determined and normalized against the individual cross sectional area of the initial sample to determine the engineering strain. The results shown in Fig. 7 indicate that PHA films can achieve elongation to break statistics of 679% and ultimate tensile strength of 21.3 MPa when the composition of $Mg_2B_2O_5$ nanowires is 0.1%. The elongation to break and the ultimate tensile strength were increased by 8.8% and 16.1% compared with those of pure PHA. This result indicates that the toughness of PHA was improved by the incorporation of $Mg_2B_2O_5$. Moreover, the Young's modulus was also improved, as can be seen through comparing the different slopes of the stress response to deformation at low strains in the curves. Therefore, the rigidity was also strengthened. When the content of $Mg_2B_2O_5$ nanowires was 0.2%, the elongation to break increased by 11.1% and the ultimate tensile strength increased by 27.2% compared with those of the pure PHA. In addition, the Young's modulus of the composites was improved. Generally speaking, the toughness will decrease with the increase in rigidity. However, both the rigid-

ity and the toughness increased when the content of $Mg_2B_2O_5$ nanowires was 0.1% and 0.2%. The Young's modulus and the ultimate tensile strength were only improved a little and the elongation at failure was reduced as the content of $Mg_2B_2O_5$ nanowires was increased to 0.3%. This indicates that the excessive addition of $Mg_2B_2O_5$ nanowires increases the rigidity but does not help to improve the toughness. Therefore, we can conclude that the usage of $Mg_2B_2O_5$ nanowires not only increases the toughness but also improves the rigidity of the PHA polymers. The optimal reinforcement mix is 0.2% $Mg_2B_2O_5$ nanowires. The $Mg_2B_2O_5$ nanowires uniformly disperse in the PHA, as can be observed in the fracture surface of the composite (Fig. 7(b)). This indicates that $Mg_2B_2O_5$ nanowires have good compatibility with PHA and that there is an intense interaction between the reinforcements and the PHA. This could effectively prevent the cracks from all directions and improve the strain strength of the composite. From the fracture surface (Fig. 7(b)), many shallow dimples can be found, which result from the top of the $Mg_2B_2O_5$ nanowires pulling out during the tensile deformation. This suggests that the interfacial strength in the composite is intense and corresponds to the high tensile strength.

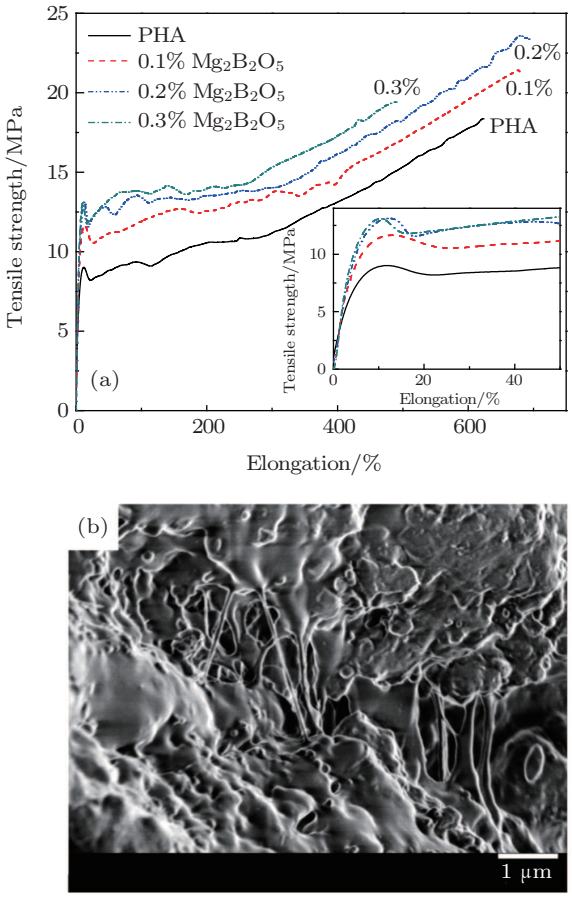


Fig. 7. (color online) (a) The stress-strain curves for polymer samples tested in uniaxial extension with strain ratio 30 mm·min^{-1} at room temperature (20 °C); (b) fracture surface of the composite (0.2% $Mg_2B_2O_5$).

4. Conclusion

In summary, PVP promotes 1D preferential growth and helps to increase the aspect ratio of the $MgBO_2(OH)$ nanowires. The synthesis of high aspect-ratio $Mg_2B_2O_5$ nanowires by the thermal conversion from $MgBO_2(OH)$ to $Mg_2B_2O_5$ at a low temperature of 700 °C has been investigated, indicating that the recrystallization process plays an important role in the protection of the 1D nanostructure. A slow heating rate (1 °C·min^{-1}) is favorable for protecting the 1D nanostructure. Uniform $Mg_2B_2O_5$ nanowires have been obtained with an average diameter of $\sim$ 30 nm, an average length of $\sim$ 15 μm, and an aspect ratio of 500. Moreover, the elongation to break and the ultimate tensile strength of the PHA composite with 0.2% $Mg_2B_2O_5$ nanowire content were increased by 11.1% and 27.2%, respectively. The rigidity was also tremendously improved. These results demonstrate the effectiveness of the $Mg_2B_2O_5$ nanowires for reinforcement applications in polymer composites. Reinforcing $Mg_2B_2O_5$ nanowires are expected to have effective applications in other materials.

References

[1] Elssfah E M, Elsanousi A, Zhang J, Song H S and Tang C C 2007 *Mater. Lett.* **61** 4358

[2] Liu J P, Li Y Y, Huang X T, Li Z K, Li G G and Zeng H B 2008 *Chem. Mater.* **20** 250

[3] Hu Z S, Lai R, Lou F and Wang L 2002 *Wear* **252** 370

[4] Chen S H, Jin P P, Schumacher G and Wanderka N 2010 *Compo. Sci. Technol.* **70** 123

[5] Christopher W J, McChalicher and Friedrich S 2007 *J. Biotechnology* **132** 296

[6] Xia Y N, Yang P D, Sun Y G, Wu Y Y, Mayers B, Gates B, Yin Y D, Kim F and Yan H Q 2003 *Adv. Mater.* **15** 353

[7] Pan Z, Dai Z and Wang Z 2001 *Science* **291** 1947

[8] Gu C Z, Luo Q, Yang H F, Jin A Z, Li J J, Wang Z L, Wang Q, Xu P, Quan B G, Yue S L, Huang Y and Shi C Y 2006 *Physics* **35** 0

[9] Zhang J and Zhao Y M 2006 *Acta Phys. Chim. Sin.* **22** 110

[10] Li Y, Fan Z, Liu J and Chang R P H 2004 *Chem. Mater.* **16** 2512

[11] Sakane K, Kitamura T, Wad H and Suzue M 1992 *Adv. Powder Technol.* **3** 39

[12] Zhang Q and Zhao Y M 2006 *Acta Phys. Chim. Sin.* **22** 110

[13] Li S, Fang X, Leng J, Shen H Z, Fan Y and Xu D P 2010 *Mater. Lett.* **64** 151

[14] Zeng Y, Yang H B, Fu W Y, Qiao L, Chang L X, Chen J J, Zhu H Y and Li M H 2008 *Mater. Research Bull.* **43** 2239

[15] Cao M H, Hu C W and Wang E B 2003 *J. Am. Chem. Soc.* **125** 11196

[16] Liu B and Zeng H C 2003 *J. Am. Chem. Soc.* **125** 4430

[17] Liu Z H, Hu M C and Gao S Y 2004 *J. Therm. Anal. Calorim.* **75** 73

[18] Liu Z H and Hu M C 2004 *Therm. Acta* **411** 27

[19] Zhu W, Zhang X, Xiang L and Zhu S 2009 *Nanoscale Res. Lett.* **4** 724

[20] Zhu W, Zhang Q, Xiang L, Wei F, Sun X, Piao X and Zhu S 2008 *Cryst. Growth Des.* **8** 2938

[21] Zhu W, Zhang Q, Xiang L and Zhu S 2011 *Cryst. Eng. Comm.* **13** 1654

[22] Lepot N, Bael M K Van, Van den R H, D'Haen J, Peeters R and Franco D 2007 *Mater. Lett.* **61** 2624

[23] Wei S F, Lian J S and Jing Q 2009 *Appl. Surf. Sci.* **255** 6978