Journal of Applied Science and Engineering Innovation, Vol.7, No.3, 2020, pp. 125-131
ISSN (Print): 2331-9062
ISSN (Online): 2331-9070

Effects of Divalent Calcium Ion on the Flame Retardancy and Pyrolysis Products of Synthetic Polyvinyl Alcohol

Li Zhenxing, Tian Xing*

College of Materials Science and Engineering, State Key Laboratory of Bio-Fibers and Eco-Textiles, Collaborative Innovation Center of Marine Biobased Fiber and Ecological textile Technology, Institute of Marine Biobased Materials, Qingdao University, Qingdao 266071, China.

Abstract: In this study, a polyvinyl ion gel containing metal ions was prepared by crosslinking acrylic acid containing metal ions with polyvinyl alcohol. The thermal cracking products and thermal stability of metal calcium ion polyvinyl alcohol/acrylic acid gel were studied by LOI, TG, FTIR, XRD, Py-GC/MS and SEM methods. The addition of metallic calcium ions increases the LOI value and enhances the flame retardancy of polyvinyl alcohol. It shows from TG result that the addition of metallic calcium ions promotes the formation of carbon layers and improves the thermal stability of polyvinyl alcohol. It was proved by FTIR, XRD and SEM that calcite-type calcium carbonate was formed on the polymer surface during the PVA/AA/Ca heating process, forming a protective layer to prevent the entry of oxygen and the volatilization of volatiles. This research is a contribution to the improvement of the thermal stability of synthetic polymers by metal ions and further application to battery separators.

Keywords: Polyvinyl Alcohol, Acrylic Acid, Calcium, Flame Retardant

INTRODUCTION

Confronting with the urgent problems of increasing depletion of resources and deterioration of the environment, it is extremely necessary to reduce the use of fossil fuels and protect the environment [Zhang, *et. al.*, 2017]. Nowadays, mobile phones, computers and electric cars are widely used in our daily life, which largely depend on the performance and development of energy storage systems [Choi, *et. al.*, 2016]. The lithium-ion batteries have the largest demand in the world by virtues of its light weight, low price, high energy density, excellent power density, long cycle lifetime and environmental friendlinesss [Li, *et. al.*, 2009]. However, high energy density lithium-ion batteries with more chemical energy may release chemical energy in the form of heat, resulting in fire or explosion [Chen, *et. al.*, 2018]. The battery separator is an important part of the battery, which insulates the anode and cathode, thus preventing the chemical energy in the battery from being transformed into thermal energy, weakening the reaction between the electrode and the electrolyte, inhibiting the release of a large amount of heat [Deng, *et. al.*, 2016]. And separator plays an indispensable role in providing the effective channels for the transmission of lithium-ions between electrodes. Currently, the polyolefin microporous membranes have become the main commercialized separators owing to their good electrochemical performance, such as polypropylene (PP), polyethylene (PE) and their combinations [Zhang, *et. al.*, 2007]. However, there is a problem of poor thermal stability, which makes the battery easily short-circuited by heat and threatens safety performance. The fiber separators have gradually become a new type of porous battery separators, such as natural cellulose separators, which exhibit excellent electrochemical performance in battery applications. Polyvinyl alcohol fiber is a commonly used synthetic fiber and can also be used in the preparation of battery separators. Due to the poor flame retardant effect of PVA fiber itself, we conducted thermal stability studies on raw materials.

PVA has a regular molecular structure, a compliant molecular chain, and a large number of hydroxyl groups [Ma, 2006]. It is a synthetic water-soluble polymer. It has the advantages of high electrolyte wettability, excellent spinnability, good mechanical properties and film-forming properties [Wang, et. al., 2018]. However, the PVA material is easily ignited in the air, and their limiting oxygen index (LOI) value is about 19% [Jiang, *et. al.*, 2017]. Therefore, the pure PVA cannot solve the thermal stability performance of the separator. It has been reported in a large number of literatures that metal ions can enhance flame retardancy of polymers such as natural alginate and cellulose [Manfredi, *et. al.*, 2006]. For this reason, PVA polymer is added acrylic acid with metal ion-containing, which solves the problem of poor thermal stability of PVA polymer and improves flame retardancy.

Herein, the polymer synthesized from polyvinyl alcohol and acrylic acid is used as the raw material, metal calcium ion is added, and then the polymerization is initiated by the 2959 photoinitiator and the BIS crosslinking agent. The gel polymer of polyvinyl alcohol and calcium acrylate was successfully prepared. The thermal stability of metal ions to unnatural water-soluble synthetic polymers was explored. The addition of metal ions enhances the thermal stability of polyvinyl alcohol and explains the flame retardant mechanism. It not only improves the flame retardant effect of metal ions in synthetic materials, but also plays an important role in lithium ion battery separators.

EXPERIMENTAL METHOD

Materials and methods

Poly(vinyl alcohol) (PVA) (Mn≈7.8×104, 98% hydrolysis degree, Sinopharm Chemical Reagent Co., Ltd, China),acrylic acid (AAc) (purified by distillation, Tianjin Beilian Fine Chemicals Development Co., Ltd. China),calcium hydroxide ($Ca(OH)_2$)(Sinopharm Chemical Reagent Co., Ltd, China), N,N'-methylenebis(acrylamide) (BIS) (Shanghai Macklin Biochemical Co., Ltd, China),2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (photoinitiator 2959)(Sinopharm Chemical Reagent Co., Ltd, China).

Preparation of polyvinyl alcohol/calcium acrylate

Acrylic acid is neutralized by calcium hydroxide to form an acrylic acid solution containing calcium ions, and then initiator 2959 (0.5 wt%) and cross-linking agent BIS (1 wt%) were added and stirred until uniform. PVA was added to a 250ml flask, placed in a constant temperature magnetic stirrer and heated to 100 ℃, kept warm and stirred for 4h to obtain a PVA aqueous solution (10wt%). After cooling to 50 ℃, the PVA aqueous solution and acrylic acid solution containing calcium ions were mixed, and the solution was stirred at 50 ℃ for 4 hours to make it uniform. The mass ratio of polyvinyl alcohol to acrylic acid in the mixed solution is 6/15, and the neutralization degree of acrylic acid is 30%, 40%, 50%, 60%. The mixed solution was transferred to a petri dish and kept under an ultraviolet lamp (20W ×6) for 20 hours, so that the calcium acrylate in the mixed solution began to chemically crosslink to form calcium polyacrylate. The petri dish was then frozen in a refrigerator at -23℃ for 24 hours, and then the frozen hydrogel was thawed at room temperature for 1 hour. The freeze-thaw process was repeated three times to obtain a double-network gel. The flowchart of the PVA/AA/Ca preparation experiment was shown in Fig. 1 in support information. The polyvinyl alcohol/calcium acrylate gels prepared with different neutralization concentrations were labeled as 30%-PVA/AA/Ca, 40%-PVA/AA/Ca, 50%-PVA/AA/Ca, 60%-PVA/AA/Ca.

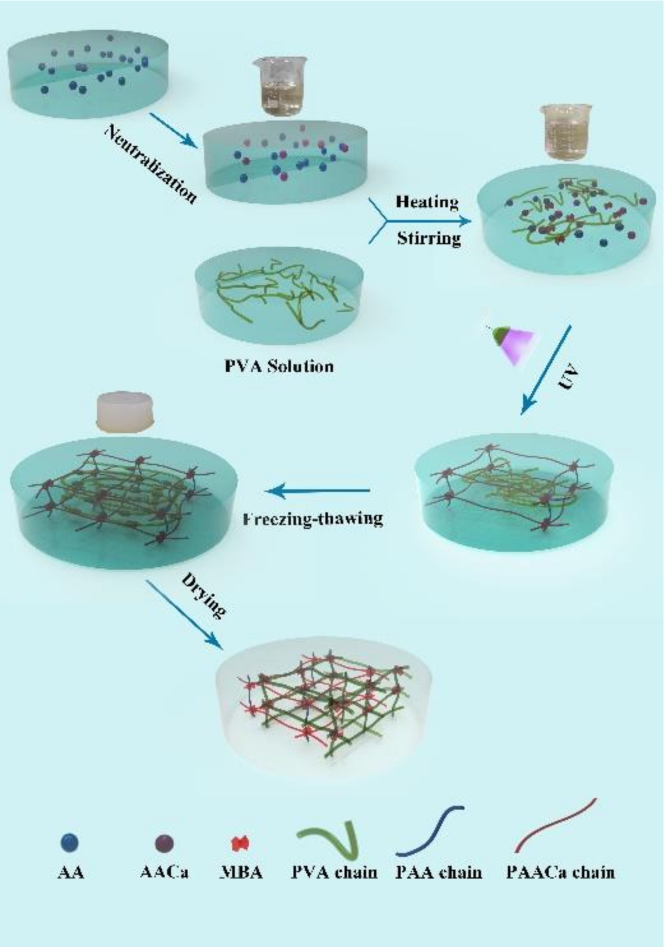


Fig.1. The flow chart of gel preparation

Methods

The infrared curves of polyvinyl alcohol calcium acrylate gel with different degrees of neutralization were measured by Vector22 FTIR spectrometer. In this experiment, the samples were measured with a scanning range of 500~4000 cm−1. Each spectrum was collected from 32 scans in the transmission mode.

The samples with a size of 100mm × 6.5mm × 3mm were prepared and the limit oxygen index (LOI) measurement was performed using HC-2 instrument made in China.

The thermal stability of polyvinyl alcohol calcium acrylate gel with different degrees of neutralization were tested by TG209F3 in a flowing nitrogen atmosphere of 20 mL/min between 50 ℃ and 600 ℃ at a heating rate of 10 ℃ /min.

The X-ray diffraction analyzer was used by DX-2700 to qualitatively analyze the sample high-temperature calcination product, and then it was determined by comparison with the standard spectrum.

The surface of the sample was observed by Quanta 250 FEG scanning electron microscope to obtain the surface morphology of the sample. First, the sample to be tested is sprayed with gold, and then placed on the sample stage of the scanning electron microscope to observe the morphology of the sample at room temperature.

The determination of the cracking products of polyvinyl alcohol calcium acrylate gel with different degrees of neutralization after 550 ℃ was tested and analyzed by Py-GC/MS method.

RESULTS AND DISCUSSION

Characterization

Infrared curves of PVA, AA and PVA/AA/Ca gels in the wavelength range of 500-4000cm^{-1} were shown Fig. 2. It can be seen that the absorption peaks at 3274 cm^{-1} was attributed to the stretching vibration peaks of -OH group in PVA and the stretching vibration absorption peak at 1705cm-1 was C=O of AA[27]. The peak at 1410 cm^{-1} in the PVA/AA/Ca curve was caused by the C-O stretching vibration peak; the band at 1450 cm^{-1} corresponded to the C-H bending vibration. The peak at 2950 cm^{-1} was due to the asymmetry of the C-H group stretching vibration. The peak at 1645cm^{-1} was the asymmetric stretching vibration of C = C. The absorption band near 1705 cm-1 disappeared, and instead it appeared absorption peaks of 1552 cm^{-1} and 1450 cm^{-1}, which corresponded to the antisymmetric and symmetric stretching vibrations of the carboxylate structure. The peak at 1144cm^{-1} and 1095cm^{-1} was the C-O-C stretching vibration absorption band of the ester[28,29]. Therefore, the PVA/AA/Ca gel was successfully prepared.

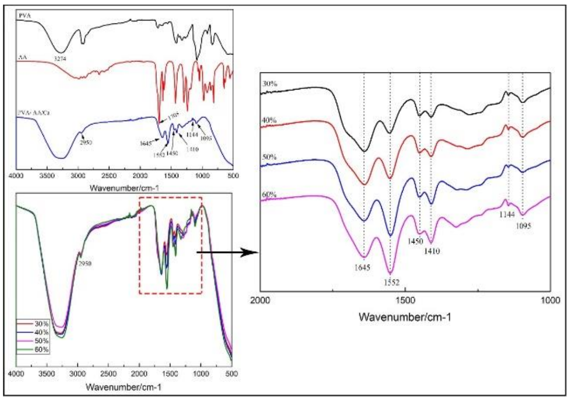


Fig. 2. The FTIR spectrum of the PVA,AA,PVA/AA/Ca

Fig. 3 showed the LOI values of polyvinyl alcohol calcium acrylate gel with different degrees of neutralization. The crosslinked acrylic acid polyvinyl alcohol polymer has a higher LOI value, and the LOI value of the PVA/AA/Ca gel added with calcium ions is higher than that of the PVA/AA gel. And the LOI value of PVA/AA/Ca gels appeared to be large with the increase of calcium ion content. It shows that the addition of metal ions greatly improves the flame retardant properties of hydrogels. This is because metal ions form carbon oxides during heating, which protects the material.

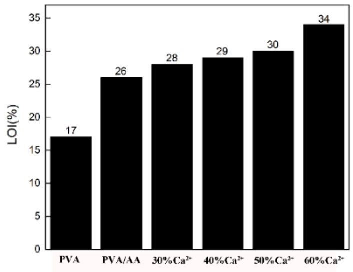


Fig. 3. PVA, PVA/AA and PVA/AA/Ca LOI values

Fig. 4(a) showed the TG curves of PVA, PVA / AA, and PVA/AA gel containing metal calcium ions in an air atmosphere. It can be seen from the TG curve of pure PVA that the decomposition of polyvinyl alcohol was divided into three stages. The first stage was below 190°C, the quality decline in this stage was mainly due to the loss of bound water. The second stage occurred at 250-350 ℃, and the PVA quality decreased sharply, which was reduced by about 70%. The main reason for the quality reduction at this stage was the elimination of water and the breaking of molecular chains. The third stage occur at 400-500 ℃, which was reduced by about 14.5%. The quality decline in this stage was due to the H2 elimination reaction[20]. When the temperature of the gel added with calcium ions was lower than 380℃, the thermal decomposition of the four hydrogels with different calcium ion concentrations was similar. Thermal decomposition can be also divided into three stages. The first stage was in the temperature range of 150-270℃, which was the decomposition of carboxyl groups in the gel. The second stage was in the range of 270-380℃, in which carbon layer and intermediate products were formed. The third stage was in the range of 400-550℃, 30%-PVA/AA/Ca polymer formed calcium carbonate material when it reached 540℃, 40% -PVA/AA/Ca polymer formed calcium carbonate at 520℃, 50%-PVA/AA/Ca and 60%-PVA/AA/Ca polymers produced calcium carbonate material at about 470℃. It was found that the polymer with more calcium ion content produced calcium carbonate at lower temperature. The polymer added with calcium ions was gradually destroyed during heating, the content of the carbon layer increased and the calcium carbonate material was gradually formed, which was laid on the surface of the polymer to protect the internal materials from further damage [Zhang, *et. al.*, 2017].

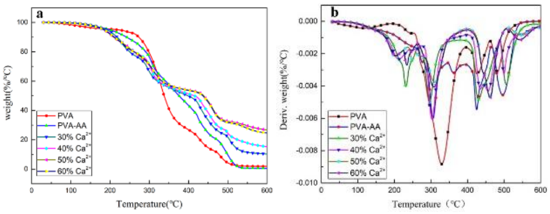


Fig. 4. TG (a) and DTG (b) curves obtained in the study of samples at a heating rate of 10 ℃ min^{-1}.

Table 1 listed the thermogravimetric analysis data of the polymer, including the initial decomposition temperature Ton, the maximum decomposition rate temperature Tmax and the carbon residues of 450℃, 550℃ and 600℃. It can be seen from Table 1 and Fig. 4(b) that the thermal degradation temperature (Tona) of the cross-linked acrylic polyvinyl alcohol gel was significantly lower than that of polyvinyl alcohol (Tona). The cross-linked acrylic polyvinyl alcohol material began to decompose at a lower temperature than the original PVA material to form a more stable structure and promote the formation of a gel carbon layer, which played a protective role in the polymer. The temperature at which the calcium ion-added gel started thermal degradation was lower. During the degradation process, the calcium ion-containing gel formed metal carbides and metal oxides, which were laid flat on the surface of the gel to isolate the heat and energy of the outside air and the matrix. Table 1 lists the residual carbon rates of gels with different calcium ion concentrations at 600 ℃ as 10.3%, 15.3%, 26.7%, and 24.7%. It was much greater than the 1.8% carbon retention rate of pure PVA materials at 600° C. Therefore, calcium ions can induce polyvinyl alcohol/acrylic polymer to produce more carbon. The data showed that calcium ions changed the thermal degradation behavior of polyvinyl alcohol/acrylic acid gel and improve its thermal stability.

Table 1. A summary of the degradation temperature and char yield of PVA, PVA/AA, PVA/AA/Ca

Sample	T_{on}^{a}(℃)	T_{max}^{b}(℃)	Char residue(%)		
			500 ℃	550 ℃	600 ℃
PVA	219.7	330.8	4.3	1.9	1.8
PVA/AA	198.8	307.2	9.7	0.63	0.5
PVA/AA /30%Ca^{2+}	190.8	297.6	21.8	11.4	10.3
PVA/AA /40%Ca^{2+}	183.7	304	24.5	17.8	15.3
PVA/AA /50%Ca^{2+}	183.7	465.1	32.6	29.6	26.7
PVA/AA /60%Ca^{2+}	183.8	465.5	31.8	27.8	24.7

Fig. 5 was the infrared spectrum of the dried 50%-PVA/AA/Ca gel sintered at different temperatures in the wavelength range of 500- 4000cm^{-1}. The characteristic absorption peaks of calcium carbonate appeared at 1792cm^{-1}, 1410cm^{-1}, 870cm^{-1} and 710cm^{-1}. The peak at 1792 cm^{-1} was formed by C=O vibration of calcite carbonate. The strong absorption peak around 1410 cm^{-1} was formed by the asymmetric stretching vibration of the C-O bond in calcite-type calcium carbonate. The peak near 870 cm-1 was the out-of-plane deformation vibration peak of CO_3^{2-}. The peak near 710cm^{-1} was formed by O-C-O in-plane deformation vibration. It is observed from Fig. 5 that when the temperatures were 250℃ and 300℃, there was a strong absorption peak around 1410 cm^{-1}, and the absorption peak at 1410 cm^{-1} decreased at 300℃ compared with 250℃. With the increase of temperature, the absorption peak intensity of 1410 cm^{-1} was gradually strengthened, the vibration peak of CO_3^{2-} out-of-plane deformation appeared at 870 cm^{-1} at 450 ℃, and the CO_3^{2-} out-of-plane deformation at 550 ℃. When the temperature was 500 ℃, the in-plane deformation vibration peak of O-C-O has appeared near 710cm^{-1}. At this temperature, the four absorption peaks of calcite-type calcium carbonate all appeared[30,31]. Obviously, it was proved that the gel polymer formed stable calcite-type calcium carbonate during heating.

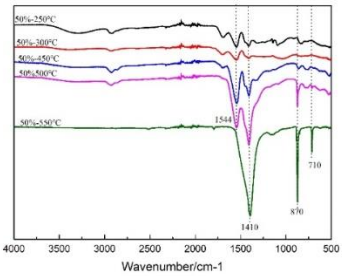


Fig. 5. The FTIR spectrum of 50%-PVA/AA/Ca polymer at different temperatures

Fig. 6 is the XRD patterns of polyvinyl alcohol/acrylic acid gels with different degrees of neutralization when heated at 250 ℃, 450 ℃, 500 ℃ and 550 ℃. The XRD patterns of gels with different degrees of neutralization at 550 ℃ were basically similar. At this temperature, a strong peak appeared at 2θ = 29.4°. This strong peak was the crystal plane diffraction peak of calcite calcium carbonate (104), which also showed that a protective layer of calcium carbonate was formed on the surface of the gel polymer during heating [Kontoyannis, *et. al.*, 2000]. By comparing the formation temperature of calcium carbonate, the PVA/AA/Ca began to produce calcite-type calcium carbonate at 500℃ to 550℃. The PVA/AA/Ca gel began to form calcite-type calcium carbonate at 450℃ to 500℃. The-PVA/AA/Ca gel produced calcite-type calcium carbonate at less than 450℃.

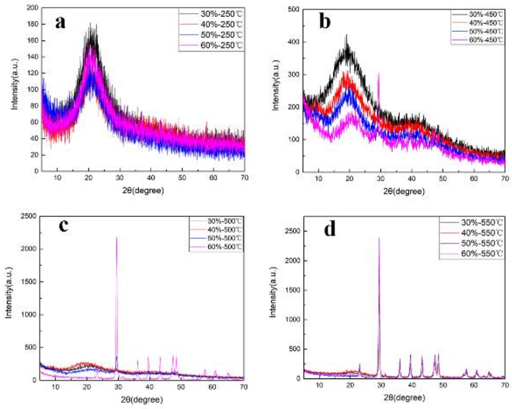


Fig. 6. XRD patterns of polymers with different calcium ion contents at different temperatures. (a) Temperature is 250 ℃ (b) Temperature is 450 ℃ (c) Temperature is 500 ℃ (d) Temperature is 550 ℃

Tables 2 and 3 list the main compounds of PVA and PVA/AA/Ca thermal cracking, and further investigated the flame retardant properties and combustion process of the samples. It can be seen from Table 2 that the polyvinyl alcohol polymer mainly produced 15 kinds of cracked products at 550 ℃, of which the content of isopentyl methyl ketone, crotonaldehyde and 2,2-dimethyl-3,4-pentadienal was the most. In all products, most of them were chain-like structures. Table 3 showed that there were 12 main cracking products of 30%-PVA/AA/Ca gel at 550 °C, while there were 7 main cracking products of 50%-PVA/AA/Ca gel at 550℃. Compared with pure polyvinyl alcohol chain cracking products, the calcium alcohol-added polyvinyl alcohol products were mainly cyclic. It showed that the addition of metal ions made the polymer more easily dehydrated to form a ring-shaped substance and promote the formation of a carbon layer. Comparing the pyrolysis products of samples with different degrees of neutralization, the pyrolysis products decreased as the degree of neutralization increases. It showed that the increase of calcium ion concentration made the degradation of polyvinyl alcohol/acrylic polymer incomplete. It is further explained that the increase in calcium ion concentration helped to form a protective layer of calcium carbonate to inhibit the decomposition of the polymer.

Table 2 Main thermal cracking products of PVA at 550 ℃

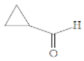
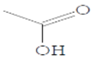
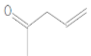
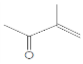
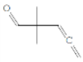
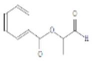
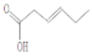
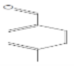
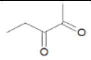
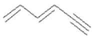
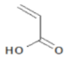
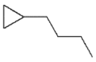
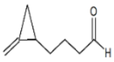
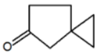
Molecular structure	Molecular formula	PVA	
		Time (min)	Area (%)
	$C_7H_{14}O$	1.757	14.9448
	C_4H_6O	2.032	5.4681
	C_4H_6O	2.486	42.7704
	$C_2H_4O_2$	2.708	3.1828
	C_5H_8O	2.848	2.0517
	C_5H_8O	3.628	2.4832
	C_6H_8O	4.579	1.4495
	C_6H_8O	5.469	2.815
	$C_7H_{10}O$	5.578	15.4849
	$C_{10}H_{10}O_3$	5.994	1.9388
	$C_6H_{10}O_2$	6.611	1.26
	C_8H_8O	6.8	1.0848
	C_9H_{14}	7.154	1.4349
	C_9H_{14}	7.256	1.1223

Table 3 The main thermal cracking products of 30% and 50%-PVA/AA/Ca at 550 ℃

Molecular structure	Molecular formula	30%-PVA/AA/Ca Time (min)	Area (%)	50%-PVA/AA/Ca Time (min)	Area (%)
	$C_5H_8O_2$	2.26	2.1609	2.27	3.2916
	C_6H_6	2.74	2.8308	2.72	2.5374
	$C_3H_4O_2$	4.44	74.1645	4.61	83.4132
	C_7H_{14}	5.37	1.1602	—	—
	$C_8H_{12}O$	6.22	1.2865	—	—
	$C_7H_{10}O$	6.3	1.696	6.15	1.1181

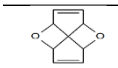
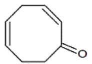
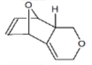
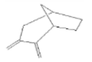
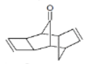
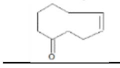
	C_8H_8O2	6.84	1.2822	6.63	1.4241
	$C_8H_{10}O$	6.9	1.3479	—	—
	$C_9H_{10}O_2$	7.1	1.971	6.87	1.0261
	$C_{10}H_{14}$	8.85	1.5077	—	—
	$C_{10}H_8O_2$	9.17	1.2578	7.08	1.196
	$C_9H_{12}O$	9.47	1.9015	—	—

Fig. 7 is an SEM image of the residue obtained by heating PVA/AA/Ca. At the temperature of 250 ℃, metal ion oxycarbon compounds were not formed, and the surface was rough and disordered. As the temperature increased, the polymer containing calcium ions gradually formed stable calcite-type calcium carbonate after being heated. At the temperature of 550 ℃, a layer of dense calcite-type calcium carbonate material was observed in Fig.7, which was laid flat on the surface of the material to block the infiltration of oxygen and inhibit the further burning of the matrix material. It showed that the addition of calcium ion had better flame retardancy for the synthetic polymer, which was consistent with the above results.

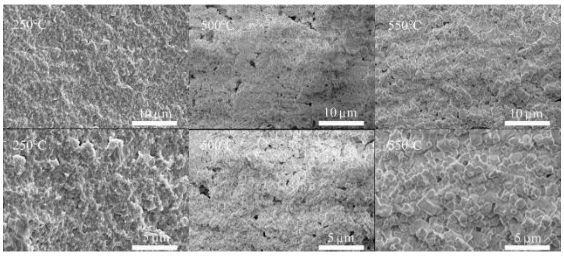


Fig.7. SEM image of hydrogel with a neutralization degree of 50% at different temperatures.

CONCLUSION

In this paper, the flammability characteristics of polyvinyl alcohol / acrylic acid gel were studied, and the thermal cracking products and thermal stability of calcium ion polyvinyl alcohol / acrylic acid gel were characterized by LOI, TG, FTIR, XRD, Py-GC/MS and SEM methods. The combustion behavior and heat resistance of the gel were studied through thermal stability test, and it was found that the addition of metallic calcium ions increased the LOI value and residual carbon content, confirming that the flame retardancy of polyvinyl alcohol was enhanced. FTIR and XRD confirmed that the gel formed metal oxycarbides during heating. The SEM image shows that metal calcium ions form calcite-type calcium carbonate on the surface of the polymer during heating, which has the effect of blocking air. The flame retardant performance and mechanism of the metal ion on the water-soluble polymer have been explored and verified.

ACKNOWLEDGMENTS

This work was supported by the National Key R&D Program of China (No. 2017YFB0309005), the Program for Changjiang Scholars and Innovative Research Team in University (No. IRT_14R30), the Taishan Scholar Program of Shandong Province (No. tspd20181208), and National Natural Science Foundation of China (No. 51603108).

REFERENCES

Arora P and Zhang Z 2004 *Battery separators Chem. Rev.* 104 4419-4462

Chen S, Zhang Z, Li L and Yuan W 2018 Covalently-bonded poly(vinyl alcohol)-silica composite nanofiber separator with enhanced wettability and thermal stability for lithium-ion battery *Chemistry Select* 3 13365-13371

Cheng X B, Zhang R, Zhao C Z and Zhang Q 2017 Toward safe lithium metal anode in rechargeable batteries: A Review *Chem. Rev.* 117 10403-10473

Choi J W and Aurbach D 2016 Promise and reality of post-lithium-ion batteries with high energy densities *Nat. Rev. Mater.* 1 359-367

Deng N, Kang W, Liu Y, Ju J, Wu D, Li L, Hassan B S and Cheng B 2016 A review on separators for lithium sulfur battery: progress and prospects *J. Power Sources* 331 132-155

Djian D, Alloin F, Martinet S, Lignier H and Sanchez J Y 2007 Lithium-ion batteries with high charge rate capacity: Influence of the porous separator *J. Power Sources* 172 416-421

Hassoun J, Panero S, Reale P and Scrosati B 2009 A new, safe, high-rate and high-energy polymer lithium-ion battery *Adv. Mater.* 21 4807-10

He H, Cai R, Wang Y, Tao G, Guo P, Zuo H, Chen L, Liu X, Zhao P and Xia Q 2017 Preparation and characterization of silk sericin/PVA blend film with silver nanoparticles for potential antimicrobial application Int. J. Biol. *Macromol.* 104 457-464

Huang B, Pan Z, Su X and An L 2018 Recycling of lithium-ion batteries: recent advances and perspectives *J. Power Sources* 399 274-286

Işik C, Arabaci G, Ispirli Doğaç Y, Deveci İ and Teke M 2019 Synthesis and characterization of electrospun PVA/Zn2+ metal composite nanofibers for lipase immobilization with effective thermal, pH stabilities and reusability *Materials Science and Engineering: C* 99 1226-1235

Jiang Y, Zhou W, Jiang M, Liu P and Xu J 2017 Flame retardant study of formalized polyvinyl alcohol fiber coated with melamine formaldehyde resins and the synergistic effect of copper ions *Polymer Degradation and Stability* 144 331-343

Jung H, Ju D, Lee W J, Zhang X and Kotek R 2009 Electrospun hydrophilic fumed silica/polyacrylonitrile nanofiber-based composite electrolyte membranes *Electrochim. Acta* 54 3630-3637

Kandola B. K, Horrocks A. R, Myler P and Blair D 2003 Mechanical performance of heat/fire damaged novel flame retardant glass-reinforced epoxy composites *Composites Part A: Applied Science and Manufacturing* 34 863-873

Kontoyannis C G and Vagenas N V 2000 Calcium carbonate phase analysis using XRD and FT-Raman spectroscopy *Analyst* 125 251-255

Kuentzel L E 1955 Calcium Carbonate as Internal Standard for Quantitative Infrared *Analysis Analytical Chemistry* 27 301-301

Levenstein M A, Anduix-Canto C, Kim Y Y, Holden M A, Nino C G, Green D C, Foster S E, Kulak A N, Govada L, Chayen N E 2019 Droplet Microfluidics XRD Identifies Effective Nucleating Agents for Calcium Carbonate *Advanced Functional Materials* 29 1808172.1-1808172.12.

Li H, Wang Z, Chen L and Huang X 2009 Research on advanced materials for Li-ion batteries *Adv. Mater.* 21 4593-4607

Li J, Li Y, Song Y, Niu S and Li N 2017 Ultrasonic-assisted synthesis of polyvinyl alcohol/phytic acid polymer film and its thermal stability, mechanical properties and surface resistivity *Ultrason Sonochem* 39 853-862

Li M, Wang X, Yang Y, Chang Z, Wu Y and Holze R 2015 A dense cellulose-based membrane as a renewable host for gel polymer electrolyte of lithium ion batteries *J. Membr. Sci.* 476 112-118

Ma K, Xiang W, Dang Y and Cai S 2006 Primary study on the assay of superficial hydroxyl group content upon the solid polyvinyl alcohol *Colloids & Surfaces B Biointerfaces* 50 72-75

Manfredi L B, Rodríguez E S, Wladyka-Przybylak M and Vázquez A 2006 Thermal degradation and fire resistance of unsaturated polyester, modified acrylic resins and their composites with natural fibres *Polymer Degradation and Stability* 91 255-261

Reig F B , Adelantado J V G and Moreno M C M M 2002 FTIR quantitative analysis of calcium carbonate (calcite) and silica (quartz) mixtures using the constant ratio method *Application to geological samples* 58 811-821

Shi R, Tan L, Zong L, Ji Q, Li X, Zhang K, Cheng L and Xia Y 2017 Influence of Na+ and Ca2+ on flame retardancy, thermal degradation, and pyrolysis behavior of cellulose fibers *Carbohydr Polym* 157 1594-1603

Wang D, Liu Y, Wang D, Zhao C, Mou Y and Wang Y 2007 A novel intumescent flame-retardant system containing metal chelates for polyvinyl alcohol *Polymer Degradation and Stability* 92 1555-1564

Wang X, Liu X, Peng S, Peng P, Zou L, Chen J and Liu J 2018 Flexible transparent flame-retardant membrane based on a novel UV-curable phosphorus-containing acrylate *Fire Mater.* 42 99-108

Wang Y, Niu J, Hou J, Wang Z, Wu J, Meng G, Liu Z and Guo X 2018 A novel design strategy for triple-network structure hydrogels with high-strength, tough and self-healing properties *Polymer* 135 16-24

Xiang Y, Li J, Lei J, Liu D, Xie Z, Qu D, Li K, Deng T and Tang H 2016 Advanced separators for lithium-ion and lithium-sulfur batteries: a review of recent progress. *ChemSusChem* 9 3023-3039

Xin S, Guo Y and Wan L 2012 Nanocarbon networks for advanced rechargeable lithium batteries *Acc. Chem. Res.* 45 1759-1769

Yin L, Xu G, Nie P, Dou H and Zhang X 2018 MXene debris modified eggshell membrane as separator for high-performance lithium-sulfur batteries *Chem. Eng. J.* 352 695-703

Zhang D, Wang J, Lin Y, Si Y, Huang C, Yang J, Huang B and Li W 2017 Present situation and future prospect of renewable energy in China *Renewable Sustainable Energy Rev.* 76 865-871.

Zhang J, Ji Q, Wang F, Tan L and Xia Y 2012 Effects of divalent metal ions on the flame retardancy and pyrolysis products of alginate fibres *Polymer Degradation and Stability* 97 1034- 1040

Zhang K, Zong L, Tan Y, Ji Q, Yun W, Shi R and Xia Y 2016 Improve the flame retardancy of cellulose fibers by grafting zinc ion *Carbohydr Polym* 136 121-127

Zhang S 2007 A review on the separators of liquid electrolyte li-ion batteries *J. Power Sources* 164 351-364