Processing Technologies of EVOH/Nano-SiO_2 High-Barrier Packaging Composites

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Abstract: The ethylene-vinyl alcohol copolymer(EVOH)/nano-SiO_2 composites were prepared by melt blending with different processing technologies(melt blending technology and film-blowing technology) and blown to film. The structure of the EVOH/nano-SiO_2 composites was analyzed through polarizing microscope (POM) and differential scanning calorimetry (DSC). The mechanical properties, barrier properties and transparency of the composites were characterized. The results showed that: different film-blowing processes can change the ordered structure and crystalline form of the EVOH/SiO_2 nanocomposites film, different blending technologies have a great effect on the structure of the composites and different processing technologies have a great effect on the properties of EVOH and EVOH/nano-SiO_2 nano-composites film.

Keywords: EVOH; nano-SiO_2; processing technology; barrier properties

1. Introduction

EVOH which has excellent barrier properties, good mechanical properties, thermal stability and transparency has a wide range of applications in packaging field [1-3]. Because of the small particle size, large surface area and the reactivity of the surface hydroxyl groups, nano-SiO_2 has predominant reinforcing and stability, and has been widely used in the plastic, rubber and other fields [4-6].

Currently, many researchers improve the barrier properties of polymer through modifying the polymer and their stresses are on the effect of chain structure of the material, crystallinity, density, chain orientation and packing state on the penetration behaviors [7-8]; the effect of the interaction of the molecular size, structure and polarity of the penetrant and the structure of the material on the permeation behaviors [9-10];the effect of polymer laminar blending or layered silicate intercalation compound with layered structure on the permeation behaviors [11-13]. In addition, they improve barrier properties of materials by blocking technology, such as multi-layer composites [14], surface treatment [15], blends [16], nanocomposites [17], etc., and prepared a series of barrier materials. However, there were few reports on controlling the processing technology to fabricate excellent barrier properties of nanocomposites. The different blown processes (extrusion speed and traction speed) can alter the EVOH/nano-SiO_2 composites membrane orientation, crystalline morphology and crystallinity, as a result the ordered structure of the composites was improved and it was more difficult for the gas molecules to pass through. The different twin-screw extruder granulation processes (processing temperature, feeding frequency, host frequency, etc.) can change the nano-SiO_2 dispersion in the EVOH and the grain morphology of composites etc. Improved crystallization properties can improve the barrier properties of polymer materials. Therefore, a reasonable controlling of EVOH/nano-SiO_2 composites processing techniques can finally obtain better properties.

EVOH/nano-SiO_2 composites were prepared by melt blending. According to our preliminary results we found blown film process has greater effects on the composites than blending process. Therefore, we first explored the blown film process. Then, under better blown film process conditions, melt blending process was explored.

2. Experimental

2.1. Primary Materials

EVOH: AT4403-type, Japan Synthetic Chemical Co., Ltd.; nano-SiO_2: 20 ~ 50 nm, self-made.

2.2. Methods

2.2.1 Film-blowing Technology Exploration

Firstly, EVOH and nano-SiO_2 were dried at 110 ℃ for 4 h and mixed at 80 ℃ for 0.5 h according to a certain proportion (mass ratio: $m(SiO_2)$: m(EVOH) = 0%, 1%, 2%, 3%, 5%) by the temperature controlling SHR-10A high-speed mixer produced by Grand Machinery Co., Ltd. Zhang jiagang; Then, the mixture was extruded and granulated by CTE-35 type (screw diameter 30 mm, aspect ratio 32) twin-screw extruder produced by BeiKeLongya Machinery Co., Ltd. Nanjing. The temperature were 190 ℃, 200 ℃, 210 ℃, 210 ℃, 210 ℃, 210 ℃, 210 ℃, 210 ℃, 210 ℃, 200 ℃. In this paper we set the temperature of metering section as a reference, the temperature of supply department decreased 20 ℃, the temperature of compressor end and die head decreased 10 ℃ respectively. The processing temperature is expressed in the temperature of metering section. When the

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nano-SiO_2 content was 5 wt%, the composites were more difficult to process, so the processing temperature is set to 220℃. Finally, the mixture was blown to film by PLD-651 type single-screw extruder produced by Germany the company Brabender. The temperature is set to 200 ℃, 210 ℃, 210 ℃, 205 ℃. When the nano-SiO_2 content was 5wt%, the processing temperature is set to 210 ℃, 220 ℃, 220 ℃, 215 ℃, and the film-blowing technology was changed (extrusion speed and traction speed) to get better EVOH/nano-SiO_2 composites film.

2.2.2 Blending Technology Exploration

Changing the twin-screw extruder granulation process (processing temperature and screw speed, etc.), the mixture was granulated according to different formulas. Then, the mixture was blown to film by Brabender single screw extruder. The film prepared from different extrusion processing was tested to get better EVOH/nano-SiO_2 composites film and blending technology.

2.3. Characterization and Testing

Film was observed by DM2500P type Polarizing Microscope of the German Leica Limited, and the crystal morphology of composites was analyzed. (Objective lens10 times, eyepiece: 50 times);

The crystallinity of the film prepared by different blowing technologies was analyzed by DSC 204C type Differential Scanning Calorimeter of the German NETZCH company. The specific steps were as follows: the temperature increasesd from room temperature to 220 ℃ at 10 ℃/min, then kept for 5 minutes at 220 ℃, and cool down to 25 ℃ at 40 ℃/min, kept for 5 minutes at 25 ℃, then heat to 220 ℃ at 10 ℃/min for a second heating. The comparison of the first and second heating of the melting enthalpy and the peak can qualitatively reflect the effect of stretching on the crystal size, that is the lager the difference of the two times higher melting enthalpy, the greater effect of the tension on the crystallization;

The tensile strength of the film was tested by XLW (L)-type PC-based intelligent electronic tensile machine of the Jinan Blue light Technical Development Center in accordance with GB13022-1991, and the tensile rate is 50 mm/min;

The light transmittance and haze of the film was tested by WGT-S-type light transmission / haze tester of Shanghai Precision Scientific Instruments according to GB2410-80;

The moisture-penetrability of the film was tested by TSY-T3 breathable apparatus of the Jinan Blue light Technical Development Centre according to GB1037-88,and the test temperature is 38 ℃,relative humidity difference is 90 ± 2%;

The oxygen permeability of the film was tested by BTY-B1-type ventilation apparatus of the Jinan Blue light Technical Development Centre according to GB1038-2000,and the test temperature is 23 ℃, relative humidity difference is 50 ± 2%.

3. Results and discussion

3.1. POM analysis of films prepared with different blowing technologies

Fig. 1 gives the POM of EVOH/nano-SiO_2 (5 wt% SiO_2) composites membrane. Fig.1 (a) corresponds to the POM of the composites membrane prepared with the extrusion speed of 10 rpm and traction speed of 3 m/min. As shown, there are big sphaerocrystals in the composite system; Fig.1 (b) is the POM of the composites film prepared with the extrusion speed of 10 rpm and traction speed of 7 m/min. In the composite system the grain size is smaller, and the number of grains increases significantly. The size of the grain is closely related to mechanical properties of films. The larger grain size leads to looser sphaerocrystals. When the material bears stress, it becomes more brittle. The tessellated grain leads to compact sphaerocrystals, which is benefit for attracting more foreign energy. More grain can increase the crystallinity of the material, thereby enhances the barrier properties of materials.

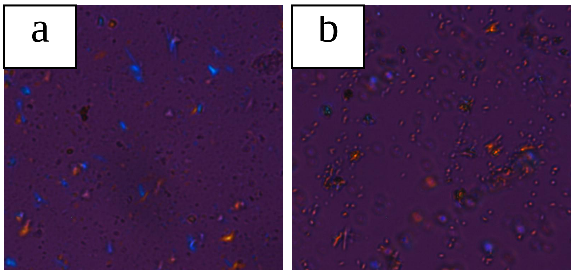

Fig.1 POM curves of the films(500 times)
a EVOH/SiO_2(5 wt% SiO_2) extrusion speed 10 rpm; traction speed: 3 m/min
b EVOH/SiO_2(5 wt% SiO_2) extrusion speed 10 rpm; traction speed: 7 m/min

3.2. DSC analysis of films prepared with different blowing technologies

Fig.2 shows the DSC curve of the pure EVOH and EVOH\nano-SiO_2 (5 wt% SiO_2) composites membrane prepared with traction speed of 7 m/min and different extrusion speeds. It can be seen that with decrease of extrusion speed, the area of crystal-melting peak, the height and width are larger. Melting range reflects the degree of perfection of polymer crystallization. Decreases of melting range indicates increase of polymer crystallize. Fig.3 is the melting heat curve with different extrusion speeds (traction speed of 7 m/min). As shown in Fig.3, with decrease of extrusion speed, caloric content becomes larger. That is to say the energy required for polymer chains disorientation, crystal solution and thermal motion of polymer chains increased. It can be seen that with decrease of extrusion speed, the arrangement of the polymer chains is more regular and the crystallinity is higher. The difference of the first melting enthalpy and the second melting enthalpy of the pure EVOH and

EVOH/nano-SiO_2 (5 wt% SiO_2) composites prepared with traction speed of 7 m/min and different extrusion speeds is shown in Fig.4. The first heating can reflect the thermal history of film itself, and the second heating can reflect the thermal history of composites. The change can qualitatively reflect the amount of the contribution of the stretching orientation and nano-SiO_2 in the crystalline.

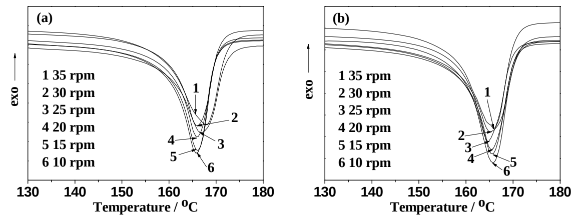

Fig.2 Influence of the extrusion speed on the melting curve of the EVOH/SiO_2 composite Film
（traction speed: 7 m/min. (a) 0 wt% SiO_2；(b) 5 wt% SiO_2）

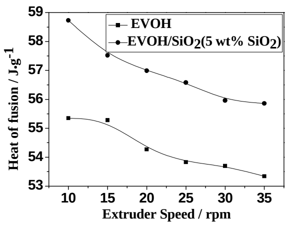

Fig.3 Influence of the extrusion speed on the fusion heat of the EVOH/SiO_2 composite film. (traction speed: 7 m/min)

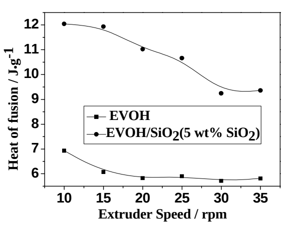

Fig.4 Influence of the extrusion speed on the differential value of fusion heat of the EVOH/SiO_2 composite film. (traction speed: 7 m/min)

3.3. The influence of film-blowing technology on the tensile strength of the EVOH/nano-SiO_2 composites membrane

The tensile strength curve of the pure EVOH and EVOH/nano-SiO_2 composites membrane with different amount of SiO_2 prepared with different extrusion and traction speeds are presented in Fig.5. It can be seen that film-blowing technology has greater effect on tensile strength. With the decrease of extrusion speed and increase of traction speed, the tensile strength increased. By the POM analysis it can be seen that the draw lead to a certain orientation of the thin films, the grain size of the nanocomposites becomes smaller and the number of grains increases significantly. The smaller grain size and more grains can improve the mechanical properties of thin films. By the XRD analysis it can be seen decrease of extrusion speed and increase of traction speed can improve the crystallinity of the polymer, and the increased crystallinity can improve the mechanical properties of thin films.

Fig.6 displays the relation schema of percentage improvement of tensile strength of the pure EVOH and EVOH/nano-SiO_2 composites membrane with different amount of SiO_2 prepared with different film-blowing technologies. It can be seen with the increase of nano-SiO2 content, percentage improvement is greater,

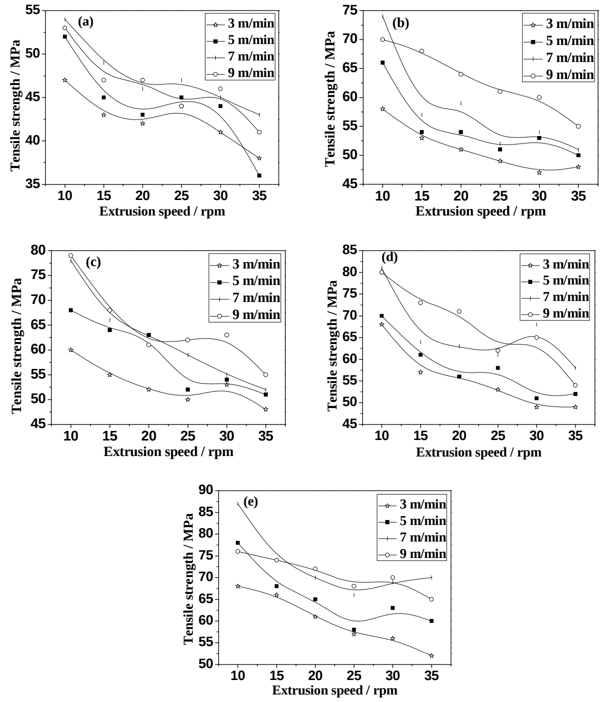

Fig.5 Influence of different film-blowing processes on the tensile strength of EVOH/SiO_2 composite film（(a) 0 wt% SiO_2; (b) 1 wt% SiO_2; (c) 2 wt% SiO_2; (d) 3 wt% SiO_2; (e) 5 wt% SiO_2)

which is becuase with the increase of nano SiO_2 content, the effect of draw on grain size and the number of grains become larger. As the nano-SiO_2 content is 5wt%, the tensile strength can be increased by 67.3%.

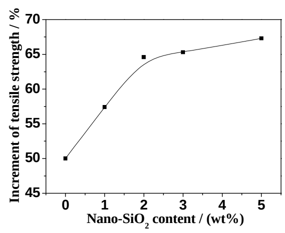

Fig.6 Influence of different amount of SiO_2 on the increment of tensile strength of the films

3.4. The influence of film-blowing technology on the moisture-penetrability of the EVOH/nano-SiO_2 composites membrane

The moisture-penetrability curve of the pure EVOH and EVOH/nano-SiO_2 composites membrane with different amount of SiO_2 prepared with different extrusion and traction speeds are shown in Fig.7. It can be seen that with decrease of extrusion speed and increase of traction speed, the moisture permeability coefficient of film has been greatly reduced. Draw makes a certain orientation of the material and the internal structure is more regular. The grain arranges closely when the grain refines and increased grain can improve the crystallinity of the material, thereby enhancing the material barrier properties.

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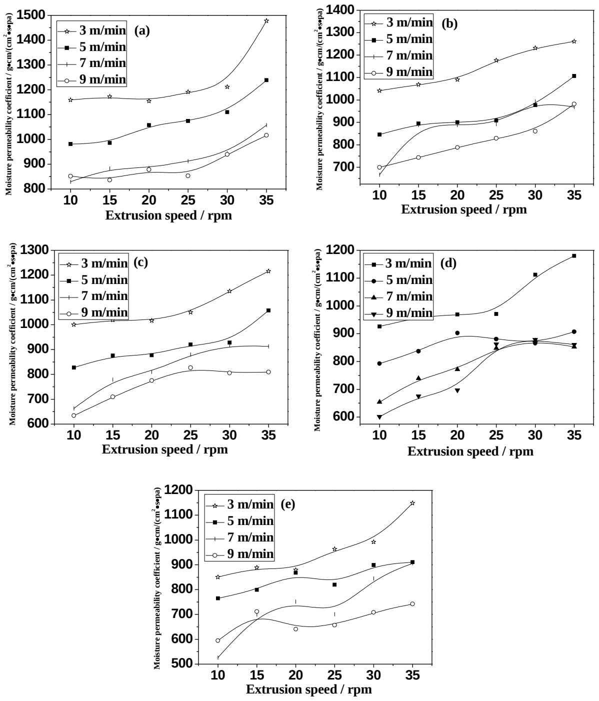

Fig.7 Influence of different film-blowing processes on the moisture permeability of EVOH/SiO_2 composite film.
((a) 0 wt% SiO_2; (b) 1 wt% SiO_2; (c) 2 wt% SiO_2; (d) 3 wt% SiO_2; (e) 5 wt% SiO_2)

Fig.8 demonstrates the relation schema of percentage reduces of coefficient of moisture permeability of the pure EVOH and EVOH/nano-SiO_2 composites membrane with different amount of SiO_2 prepared with different film-blowing technologies. As shown in Fig.8, as the nano-SiO_2 content is 5wt%, the coefficient of moisture permeability reduced by 54.2%.

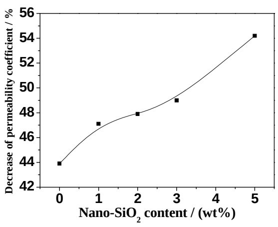

Fig.8 Influence of different amount of SiO_2 on the decrease of permeability coefficient of the films

3.5. The influence of film-blowing technology on the oxygen permeability of the EVOH/nano-SiO_2 composite membrane

Fig.9 and Fig.10 exhibit the permeability coefficient curve of the EVOH/nano-SiO_2 composites membrane (5 wt% SiO_2) prepared with different extrusion and traction speeds. It can be seen that with decrease of extrusion speed and increase of traction speed, the permeability coefficient of film has been greatly reduced. Regular arrangement of the molecular chain of film and increased crystallinity improve the barrier properties.

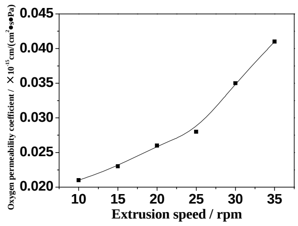

Fig.9 Influence of the extrusion rate on the oxygen permeability of the composite film (5 wt% SiO_2), traction speed: 7 m/min

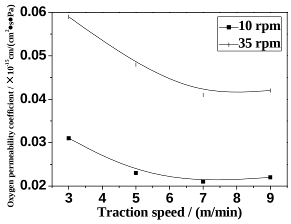

Fig.10 Influence of the traction speed on the oxygen permeability of the EVOH/SiO_2 composite film. (5 wt% SiO_2)

3.6. The influence of film-blowing technology on the transparency of the EVOH/nano-SiO_2 composite membrane

Fig.11 and Fig.12 give the light transmittance and haze curve of the EVOH/nano-SiO_2 composites membrane (5 wt% SiO_2) prepared with different extrusion and traction speeds. It can be seen that with decrease of extrusion speed and increase of traction speed, the optical property of film has been improved. Partical size of nano-SiO_2 and the size of grain also affect nanocomposites transparency. From Fig.1 it can be seen, with decrease of extrusion speed and increase of traction speed, the grain is more refining, therefore, the optical performance is improved.

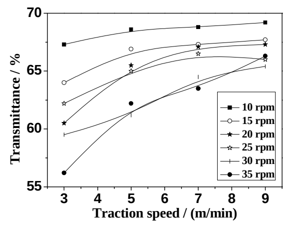

Fig.11 Influence of different film-blowing processes on the transmittance of the EVOH/SiO_2 composite film

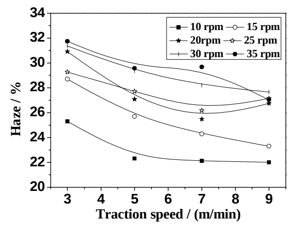

Fig.12 Influence of different film-blowing processes on the haze of the EVOH/SiO_2 composite film.

3.6. The influence of melt blending process of EVOH/nano-SiO_2 composites on product performance

Fig.13-Fig.16 show the tensile strength, moisture permeability, light transmission and haze of the pure EVOH film and composites film with different content of nano-SiO_2 blown at different temperatures (we set the temperature of metering section as a reference, the temperature of supply department decreases 20 ℃, the temperature of compressor end and die head decreases 10℃ respectively. In this paper, the processing temperature is expressed in the temperature of metering section). It can be seen that with increase of temperature, the composites' tensile strength and moisture resistance properties are improved, however, when the temperature exceeds a certain value,

the properties of composites decreases. This is because that when the processing temperature is low, on one hand, the plasticity is poor and there are infusible large spherulites; on the other hand, at the low temperature, materials are mixed unevenly and nano-SiO_2 distributes unevenly, which harms the properties of the composites; Also, at low temperature, crystal nucleation rate is high and growth rate is low, crystallinity is low, which also affects the composites' properties to a certain extent. When the processing temperature is too high, the lower molecular weight components of the material degrade and the tensile strength, moisture resistance properties and transparency decrease, the yellow index increases. So, the appropriate processing temperature is important for the preparation of EVOH/nano-SiO_2 composites.

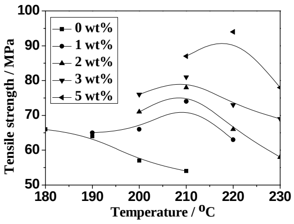

Fig.13 Influence of processing temperature on tensile strength of composites

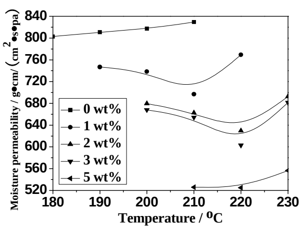

Fig.14 Influence of processing temperature on moisture permeability of composites

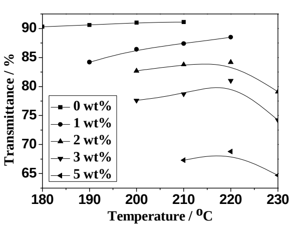

Fig.15 Influence of processing temperature on transmittance of composites

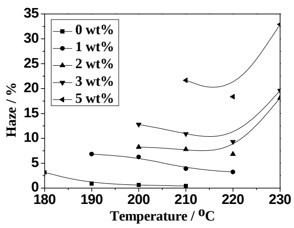

Fig.16 Influence of processing temperature on haze of composites

Fig.17 and Fig.18 are the influence of screw speed on the tensile strength and moisture permeability of EVOH/nano-SiO_2 composites (5 wt% SiO_2) at 220 ℃ respectively. It can be seen that when the screw speed is below 70 r/min,with the increase of screw speed, the films' tensile strength and barrier property are improved, coefficient of moisture permeability is decreased, but with further increased screw speed, tensile strength decreases and coefficient of moisture permeability increases. This is because when the speed is too low, the shear force is not enough and materials are mixed unevenly and nano-SiO_2 distributes unevenly; when speed is too high, filler and matrix mesh structure is damaged, which harms the properties of composites. In addition, with increase of extrusion rate, the time of roll package of materials is reduced, stress has induced polymer melt nucleation, nucleation generation time is decreased and the number of crystal nucleus increases, the spherulite size is reduced, which helps increase the composites properties.

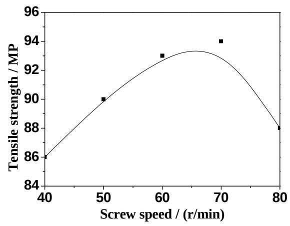

Fig.17 Influence of screw speed on tensile strength of composites

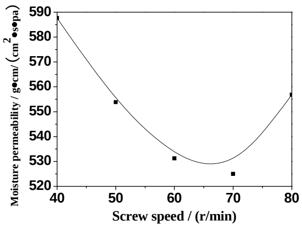

Fig.18 Influence of screw speed on moisture permeability of composites

4. Conclusion

(1) Pure EVOH and EVOH/nano-SiO_2 composite films were prepared by blow molding method. The film's orientation can be improved by changing the blown film process (reducing the extrusion rate, increasing the pulling speed), so that the grain size of nanocomposites become smaller and the number of grain increases, which significantly improve the crystallinity of the materials and the degree of molecular chain order, the film's properties has been significantly improved. When the SiO2 content is 5wt%, the coefficient of moisture permeability decreases by 54.2%; permeability coefficient decreases by 64.4%; tensile strength increases by 67.3%; light transmittance and haze has also been improved.

(2) Comprehensive of film performance testing, the better processing temperatures of EVOH/nano-SiO_2 composites with nano-SiO_2 content of 0%, 1%, 2%, 3%, 5% are 180 ℃, 200 ℃, 210 ℃, 210 ℃, 220 ℃ respectively. In the extrusion granulation process, when the screw speed is 70 r/min, the properties of material were better.

5. Acknowledgment

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