POSS Modified Polylactic Acid Film

Gu Wenjuan[1] He Zifen[1] Zhang Xiaohui[2]

([1] *Faculty of Mechanical and Electrical Engineering, Kunming University of Science and Technology, Kunming, Yunnan* 650500, *China*
[2] *Hangzhou Dianzi University, Hangzhou, Zhejiang* 310018, *China*)

Abstract POSS-NH_3Cl is introduced to polylactic acid (PLLA) by blending and grafting separately to improve the properties of PLLA, especially the transparency. A series of star-shaped polylactic acid is synthesized using L-lactic acid (L-LA) and octa (γ-chloroammoniumpropyl) octasilsesquioxane (POSS-NH_3Cl) in the presence of stannous (II) octanoate [$Sn(Otc)_2$] catalyst, and the mechanism is studied. Meanwhile, a series of composite cross-linked films are prepared by casting. The structures of these dendritic polymers are characterized by Fourier transform infrared spectra (FTIR), which conforms the presence of the grafting reaction at the same time. Ultraviolet (UV)-visible light transmittance analyzer is used to analyze the transparency of the composite films. It is found that polyethylene glycol (PEG) has little relation to the transparency of the film while the content of POSS-NH_3Cl affected the transparency. The grafted products exhibit superior transparent property than blend ones due to better compatibility with the PLLA. The transparency of the film improves even 40% in some wavelength, which is explained theoretically.

Key words materials; transparency; casting; polylactic acid

OCIS codes 070.2575; 070.4560; 070.4790; 120.7000; 160.4760

POSS 改性聚乳酸膜

顾文娟[1] 何自芬[1] 张晓惠[2]

([1] 昆明理工大学机电学院, 云南 昆明 650500; [2] 杭州电子科技大学, 浙江 杭州 310018)

摘要 将 POSS-NH_3Cl 用于聚乳酸的改性,分别以共混和接枝的方式进行添加,提高了聚乳酸膜的透明度。利用 L 乳酸和 POSS-NH_3Cl 作为原料,辛酸亚锡作为催化剂,制备了一系列的星形聚合物,并研究了其反应机理。同时,通过流延法制备了一系列复合交联膜。采用傅里叶变换红外光谱对其结构进行表征,通过对特征峰进行分析,证实了接枝反应的存在。并采用紫外-可见光谱仪对其透明度进行了研究。研究发现,PEG 对其透明度的影响不大,POSS-NH_3Cl 含量对交联膜的透光度有一定影响,且接枝产物因相容性佳,其膜的透光性亦优于共混膜。随着 POSS-NH_3Cl 含量的增加,交联膜的透光率明显增加,在某些波段透光率甚至可以提高 40%,并从理论上解释了这一现象。

关键词 材料; 透明度; 流延法; 聚乳酸

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1 Introduction

Poly L-lactic acid (PLLA) is a renewable thermoplastic polymer, which has attracted a lot of attentions in medical, agricultural, packaging, and general-purpose plastics fields because of its excellent properties such as biodegradability, biocompatibility[1-5]. However, its relatively poor mechanical property and thermal stability have limited its further practical application. In order to overcome these disadvantages, copolymer synthesis, polymer blending, and reinforced composite methods have been developed not only by using organic polymers or inorganic substances[6-7] but also by using nanocomposites[8-14] to modify PLLA in recent years. It has been found that carbon nanotubes (CNT) accelerated the crystallization rate of PLLA, enhanced the hydrolytic degradation of PLLA, and also improved the mechanical, electrical, and thermal properties of the blending of PLLA and CNT[15-17]. However, the transparency properties are more or less degraded by these methods.

In recent years, polyhedral oligomeric silsesquioxanes (POSS) as a new generation of nano-filler, has been broadly used to reinforce the comprehensive properties

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作者简介: 顾文娟(1985—),女,博士,讲师,主要从事包装材料方面的研究。E-mail: guwenjuan@whu.edu.cn

of PLLA. And numerous researches have shown that POSS can greatly improve comprehensive properties of PLLA composites compared with other inorganic nano-fillers[17-19]. Up to the present, the method that blending PLLA with POSS has been studied[18-19], only a few studies on POSS grafting with PLLA has been reported[19]. In the reference[20], POSS-PLA (polylactide tethered with POSS) is synthesized via the ring-opening polymerization of L-lactide with 3-hydroxyproxylheptaisobytyl POSS, and then the properties of PLLA blended with POSS-PLA are studied. Though the results showed that the properties of the composites could be improved by blending PLLA with POSS, the reinforced properties of the blends are limited. Because the direct mixing of inorganic materials and organic materials is thermodynamically immiscible as it is not immiscible in polymerization. And the new resultant product can not only retain excellent characteristics of the original matrix but also gain new features which can improve the defect of the original matrix[21-23].

In this work, star-shaped polylactic acid with polyhedral oligomeric silsesquioxane (POSS-g-PLLA) are synthesized via in situ polymerization method, and the structures and properties of these composites are characterized by Fourier transform infrared spectra (FTIR), and UV-visible light transmittance analyzer, respectively[24-25]. Subsequently, composite film with and without POSS-g-PLLA are prepared. And their properties are also characterized and analyzed theoretically.

2 Experimental section

2.1 Materials

L-LA (optical purity≥97%, concentration = 88 wt%, purchased from Shenzhen Brightchina Industry Co. LTD) is used after distilling to eliminate the water under vacuum 7 h at the temperature of 70 ℃. $Sn(Oct)_2$ (A. R), polyethylene glycol (PEG) (weight molecular = 600, C. R), dibutyltin dilaurate (A. R) and Ethanol (A. R) are purchased from Chemical Reagent Co. Ltd.. Chloroform (A. R) and tetrahydrofuran (THF) (A. R) are obtained from Shanghai Experiment Reagent Co. Ltd. Toluene diisocyanate (TDI, A. R) is purchased from Wuhan City Jiangbei Chemical Reagent Co., Ltd. And these materials are used without further purification. Octa (γ-chloroammoniumpropyl) octasilsesquioxane ($POSS\text{-}NH_3Cl$) is synthesized according to the method described in the literature[26].

2.2 Synthesis of PLLA, POSS-g-PLLA, composites films without and with POSS-g-PLLA

20.00 g of L-LA and 0.02 g of $Sn(Oct)_2$ are charged into a 100 ml three-necked flask, which is equipped with a magnetic stirrer. The reaction mixture is heated to 130 ℃ for 4 h under vacuum, and then the reaction mixture is continued to heat to 170 ℃ to maintain the reaction for 8 h. A viscous product is obtained. Appropriate amount of chloroform is added to the as-obtained product. After adding a certain amount of ethanol to the reaction mixture, a white powder can be obtained by washing with ethanol for 3～5 times and drying at 70 ℃ in vacuum oven.

1.00 g of $POSS\text{-}NH_3Cl$, 20.00 g of L-LA and 0.02 g of $Sn(Oct)_2$ are charged into a 100 ml three-necked flask, which is equipped with a magnetic stirrer. And then the mixture is reacted at the same reaction conditions as the stated above. The reaction between $POSS\text{-}NH_3Cl$ and L-LA is presented in Fig. 1. The resultant products are treated under the same conditions as that of synthesis of PLLA.

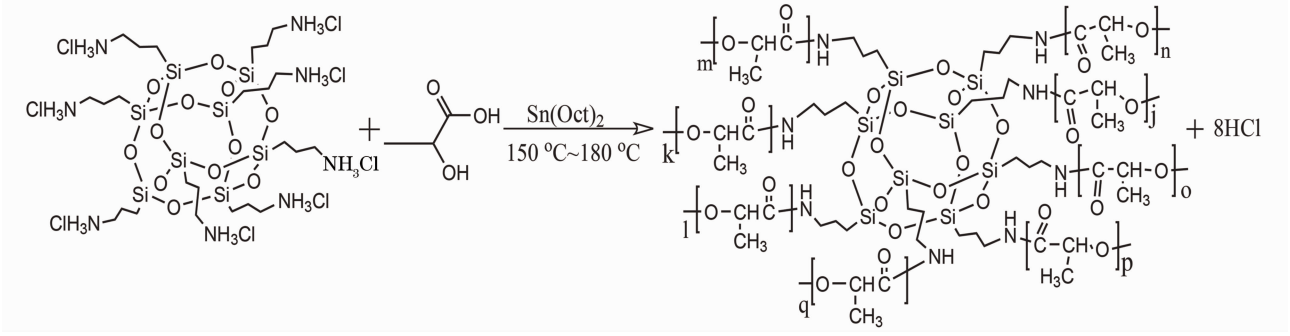

Fig. 1 Reaction between $POSS\text{-}NH_3Cl$ and L-LA

The procedure for preparation of films without POSS-g-PLLA is as follows. 4.00 g of PLLA and 20.00 g of chloroform are charged into a 100 ml flask, which is equipped with a magnetic stirrer. After the mixture is fully dissolved, 1.20 g of TDI and 0.02 g of dibutyltin dilaurate are added into the mixture, which is stirred at 80 ℃ for 5 h by magnetic stirrer. Then 4.00 g of PEG, 2.40 g of TDI and 0.02 g of dibutyltin dilaurate are charged into the reaction mixture, which is stirred at 80 ℃ for 5 h by magnetic stirrer. After cooling to room temperature, the mixture is poured into a Teflon mould subsequently, and cured for about 1 d at room temperature to give an about 0.5 mm thick sheet of films with smooth surface.

The procedure for preparation of composite films with POSS-g-PLLA is as follows. 4.00 g of POSS-g-PLLA and 25.00 g of chloroform are charged into a 100 ml flask, which is equipped with a magnetic stirrer. After the

mixture is fully dissolved, 1.20 g of TDI and 0.02 g of dibutyltin dilaurate are charged into the mixture, and the obtained mixture is stirred at 80 ℃ for 5 h by magnetic stirrer. Then 4.00 g of PEG, 2.40 g of TDI and 0.02 g of dibutyltin dilaurate are charged into the reaction mixture, and the mixture is stirred at 80 ℃ for 5 h by magnetic stirrer. After the mixture is cooled to room temperature, the mixture is poured into a Teflon mould subsequently, and cured for about 1 d at room temperature to give a film with smooth surface.

2.3 Characterizations

FTIR are recorded on Nicolet AVATAR 360FT infrared analyzer. KBr powder is used as a nonabsorbent medium. A series of samples are ground with KBr to make a 0.5 wt% mixture and pressed into a disk. And then the spectra of samples are collected and the FTIR are recorded from 4000 cm^{-1} to 400 cm^{-1}.

The transparency of cross-linked film is studied by ultraviolet (UV)-visible light transmittance analyzer (WD-9403C) within the test range of 200～800 nm.

3 Results and discussion

3.1 Structure of PLLA, POSS-NH_3Cl, POSS-NH_3Cl/PLLA and POSS-g-PLLA

FTIR for the PLLA, POSS-NH_3Cl, PLLA/POSS-NH_3Cl, and POSS-g-PLLA are shown in Fig. 2. 3460 cm^{-1} is characteristic peak of the hydroxyl group. The peak at 1460 cm^{-1} is attributed to methyl. The peak at 1380 cm^{-1} is assigned to the methane groups. 1760 cm^{-1} is the stretching vibration of carbonyl groups. 3000 cm^{-1} and 2940 cm^{-1} are the stretching vibration of C-H. 1190 cm^{-1}, 1140 cm^{-1} and 1090 cm^{-1} are the C-O-C stretching bands[27-28]. For the FTIR of POSS-NH_3Cl, the broad peak around 3020 cm^{-1} can be ascribed to the asymmetric stretching vibration of $-NH_3^+$ [29], and the peak at 1600 cm^{-1} is ascribed to the asymmetric NH_3^+ deformation vibration. The peak at 1500 cm^{-1} is the stretching vibration of N-H. The peak at 1111 cm^{-1} is ascribed to the Si-O-Si stretching vibration[30]. It is seen that after the reaction, some new peaks appear in the POSS-g-PLLA. The newly emerged peaks at 1660 cm^{-1} and 1542 cm^{-1} show the existence of NH-C=O, which is absent in POSS-CH_3Cl/PLLA. In the FTIR, it can be seen that the stretching vibration of carbonyl groups is 1751 cm^{-1} and the stretching vibration of $-NH_3^+$ is 3009 cm^{-1}, and the absorption peak is broadened. Therefore, the carbonyl groups of PLLA and the $-NH_3^+$ of POSS-NH_3Cl formed hydrogen bond[31-32]. 1604 cm^{-1} is the bending vibrations of N-H.

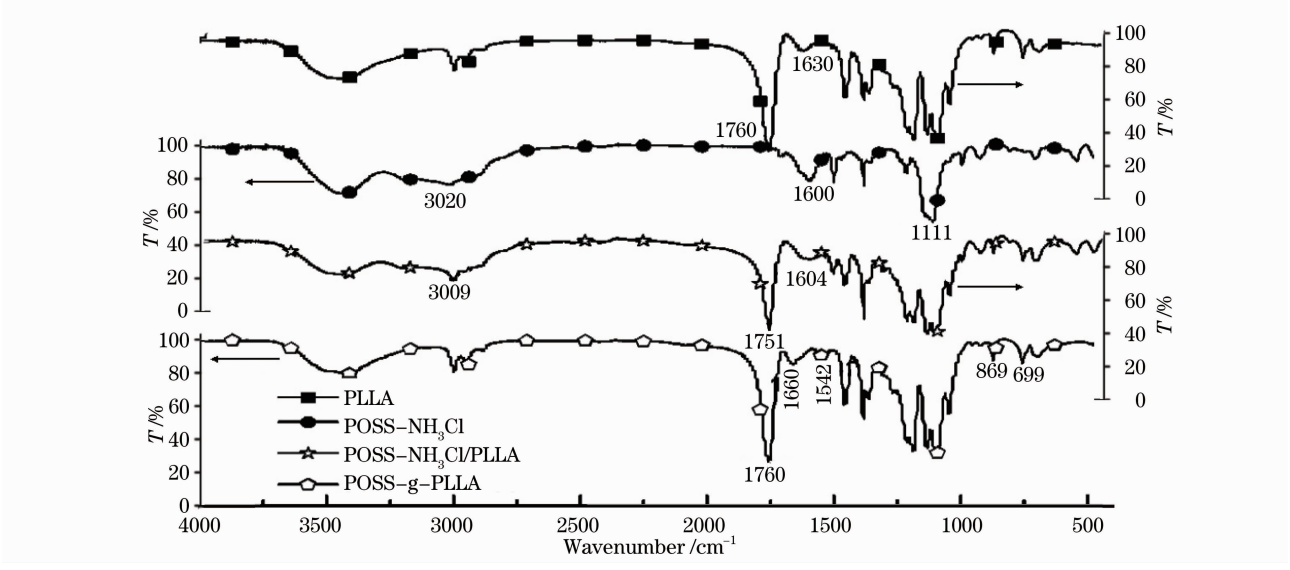

Fig. 2 FTIR spectrum of PLLA, POSS-NH_3Cl, POSS-NH_3Cl/PLLA and POSS-g-PLLA

In summary, the above IR spectra have confirmed that the secondary amide exists in the POSS-g-PLLA, and only hydrogen bond appeares in the POSS-NH_3Cl/PLLA. The secondary amide likely result from the chemical reaction between POSS-NH_3Cl and L-LA.

3.2 Transparency of composite cross-linked film

The composite cross-linked films are characterized on UV-visible light analyzer in order to study the optical properties of PLA film. The results are shown in Fig. 3 and Fig. 4.

It can be seen from the results that all the films were high transparent in the visible spectral range. And PEG content in the cross-linked film has little effect on the light transmittance. However, the transmittance of composite cross-linked film increases with increasing content of POSS-NH_3Cl. The transmittance improves even 40% during the 250～330 nm. The phenomenon could be explained as follows[33]: the transmittance of polymer is affected mainly on their structures, crystalline and so on. POSS-NH_3Cl nanoscale material is compatible with polymer. And the POSS-g-PLLA, synthesized with POSS-NH_3Cl and L-lactic acid,

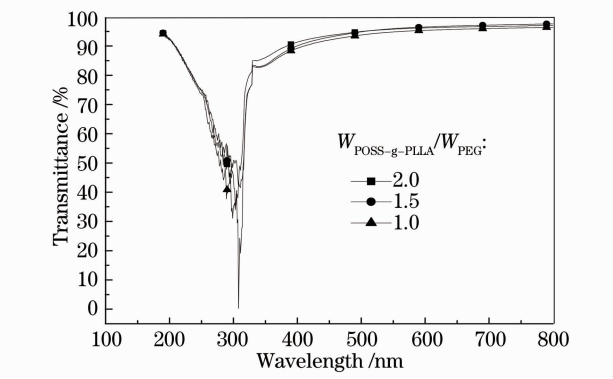

Fig. 3 Effect of PEG on transparency of composite POSS-g-PLLA cross-linked film

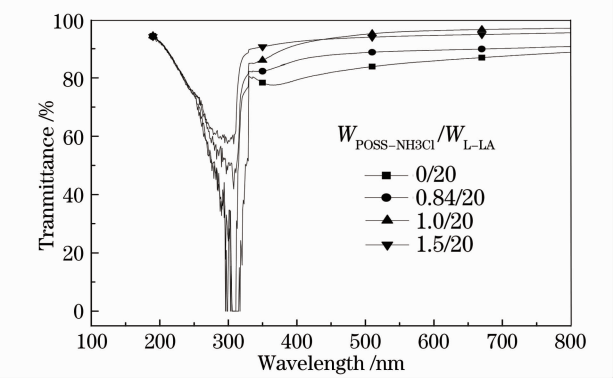

Fig. 4 Effect of POSS on transparency of composite POSS-g-PLLA cross-linked film

possesses cage-type structure. So the light could easily pass, thus increasing its transparency.

4 Conclusion

Star-shaped POSS-g-PLLA is synthesized via L-LA and POSS-NH_3Cl. Meanwhile, the structures and properties of these dendritic polymers are characterized by FTIR and UV-visible light transmittance analyzer. It is found that PET has little relation to the transparency of the film while the content of POSS-NH_3Cl affects a lot with the transparency. The transparency of the film improves even 40% during 250 ～ 330 nm. This phenomenon is explained theoretically.

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