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The Assembly of C60 in Semicrystalline PLLA Matrix

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Abstract: It has increasingly become a research focus to build higher structure composed of C60. However, there has been very few reports on the influence of polymer addition on the self-assembling behavior of fullerene in organic solvents. In this research, big needle-like C60 assemblings have been obtained in the form of PLLA/C60 composites. The largest C60 needles can be observed by naked eyes. The amount of C60 in the composite influences the length of C60 needles to some extent. DSC results indicate C60 accelerates the crystallization and lift the relative crystallinity of PLLA matrix. the results also imply the addition of semicrystalline PLLA influence the assembling behavior of C60. *i.e.*, the crystallization of PLLA accelerated by C60 also act a driving force for the enriching and the linear assembling of C60 in PLLA matrix via Van der Waals force.

Keywords: C60; Poly (L-lactide acid) (PLLA); Assembling

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Introduction

It has become one research focus to build higher structure composed of C60 fullerene. Novel low-dimensional materials of fullerenes have been extensively investigated up to now. For example, Nakanishi et al. have successfully prepared spherical vesicles, fibers, discs, cones by the self-assembly of fullerene derivatives in mixed solvents [1]. In addition, fullerene nanowiskers, nanowires or nanorods [2-4] have also been fabricated.

The development of aggregates with different morphologies and its aggregation mechanism in solution using well-defined polymeric system are of potential interest to the research community. The self-assembly of polymer-branched C60 have been reported in organic or aqueous solvents [5-8]. However, there are few reports describing the influence of polymer addition on the self-assembling behavior of fullerene in organic solvents [9,10].

Biomass-derived poly (L-lactide acid)(PLLA) has been intensively explored because it is biodegradable, compostable, producible from renewable resources, while at the same time nontoxic to human body and environment. The enhancement of crystallinity with the aid of a nucleating agent is commercially advantageous to improve the mechanical properties and thermal stability of PLLA. It has been found that C60 is effective for accelerating both the cold and melt crystallization of PLLA, and the nucleating effect of C60 is even higher than that of montmorillonite and polysaccharides [11].

In this paper, C60 and PLLA were mixed by solution method, needle-shaped C60 assemblings were found in resultant PLLA composites. The morphology and chemical composition of the C60 needles were studied by optical microscope, scanning electron microscope (SEM) and energy dispersive spectra (EDS). The influence of C60 on the crystallization behavior of PLLA was also investigated through DSC technique. The lin-

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ear assembling mechanism of C60 in PLLA during the solvent evaporation was proposed.

Experimental

Materials

Natureworks PLLA 2002D (number-average molecular weight (Mn)=1.8×10^5, weight-average molecular weight (Mw)=3.2×10^5, Mw/Mn=1.78) was supplied by Cargill Dow LLC, USA. C60 was kindly supplied by NIMS (national institute for materials science) in Japan.

Preparation of PLLA/C60 composites

The PLLA/C60 composites were prepared by the solution mixing method using dichloromethane (H_2CCl_2) as a solvent at 25℃. The solutions were prepared by dissolving PLLA and C60 in some H_2CCl_2, respectively. Then, the PLLA solution and C60 solution were mixed in a tube and homogenized by ultrasonication for 2 min. After that, the mixed solution was kept still and let the solvent evaporate very slowly until the composite film was dry. The obtained films were then further dried at room temperature in vacuum oven for 8hrs. PLLA composites containing 0.5 wt %, 1 wt % and 2wt % of C60 were prepared.

Characterizations

The resultant PLLA/C60 composites were put on the sample platform and observed by using a stereoscopic zoom microscopic Nikon SMZ 1500(Nikon corporation, Japan). In order to study the morphology and composition of the C60 needle, the PLLA in composites were etched by some H_2CCl_2, one typical C60 needle without PLLA matrix was fixed onto copper grid followed by gilding, the microstructure and chemical composition of the C60 fiber were then studied by JSM7500F and its INCA EDS accessory. Thermal analysis was carried out on a DSC from TA Instruments (model DSC 2920). About 5 mg samples was weighed and sealed in an aluminum pan. The samples were heated to 200℃ at 10℃/min and maintained for 5 min, then quenched to 0℃ at −50℃/min and maintained for 5min, and then reheated to 200℃ at 10℃/min and maintained for 5min and the second heating curves are recorded. The melting enthalpy change was recorded to study the effect of C60 on the crystallinities of PLLA during the evaporation of solvent. The standard melting enthalpy value of fully crystallized PLLA is 93.6 J/g, the relative crystallinity (Xc) of PLLA could be calculated in the following equation:

$$X_C = (\Delta H_m/93.6) \times 100\% \quad (1)$$

ΔH_m referred to the melting enthalpy change.

Results and discussions

Morphology of C60 assemblings in PLLA matrix

Stereoscopic microscope image in Fig. 1 showed the assembled C60s in PLLA matrix were like black straight needles. The amount of C60 in PLLA matrix have some influences on the length of assembled C60 needles, e.g., the black needles in PLLA composites with 1wt% C60 was longer than those in PLLA composites containing 0.5wt% or 2wt% C60, and the C60 needles in PLLA composites containing 2wt% C60 were longer than those in PLLA composites containing 0.5wt% C60. The length distribution of black C60 needles in Fig. (a), Fig. (b) and Fig. (c) was 60-110 μm, 300-500 μm, and 200-300 μm, respectively. The longest C60 needle in PLLA composites could reach over 1 cm long and could be easily seen by naked eyes. One typical C60 needle

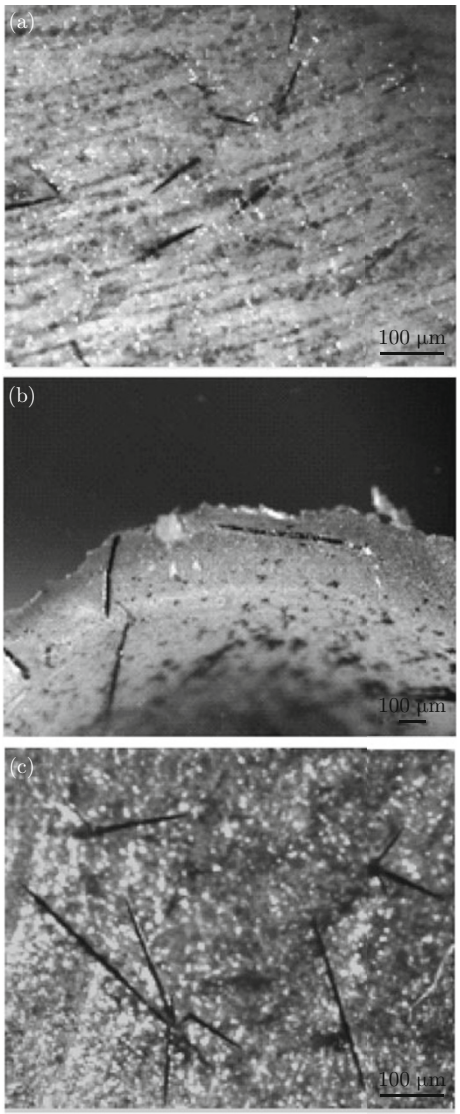

Fig. 1 Stereoscopic microscope images of PLLA films with (a) 0.5wt%, (b) 1.0%wt% and (c) 2.0wt% C60, respectively.

separated from the PLLA filled with 1wt% C60 was further studied by SEM and showed a diameter of about 50 μm and a length of 1.6 mm in the SEM image (Fig. 2).

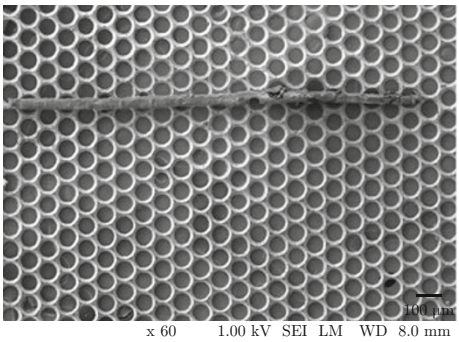

Fig. 2 SEM image of one C60 needle in PLLA composites containing 1wt% C60.

EDS analysis

To make sure whether the black needles were made up of C60, the chemical composition of the C60 needle were further analyzed via EDS. The analysis results of C60 needles in PLLA composites with 1wt% C60 indicated the black needle contained 88.1wt% (95.62atom percent) carbon element and 11.9wt% (4.58atom percent) chlorine element, which implied the needle was mainly assembled by C60 molecules. The chlorine element might come from the residual solvent absorbed or trapped by C60 molecules during evaporating.

DSC analysis

C60, as an heterogeneous nucleating agent for PLLA matrix, could induce the PLLA molecules to crystallize during solvent evaporation, in turn, the crystallization of PLLA might also influence the assembling of C60 and the formation of C60 needles. DSC characterization was carried out to study the nucleation action of C60 on PLLA molecules. The melting enthalpy change during the second heating process was recorded to study the effect of C60 on the crystallinity of PLLA matrix. As is shown in Fig. 3 and Table 1, no cold crystallization happened during the second heating process of neat PLLA, the melting peak top temperature of PLLA crystallites formed and the relative crystallinity (X_c) of PLLA was 151.2℃ and 0.75%, respectively. In the case of PLLA containing 1.0wt% C60, there is an obvious cold crystallization process that starts at 127.4℃, which indicates the nucleation action of C60. Due to the nucleation effect of C60, the PLLA in composites crystallized faster thus, the melting peak top temperature of PLLA crystallites in composites was about 0.3℃ higher than that of neat PLLA, indicating there was a slight increase in the thickness of PLLA crystallites. What is more, the X_c of PLLA in composites increased sharply to 7.06%, about nine folds higher than that of neat PLLA.

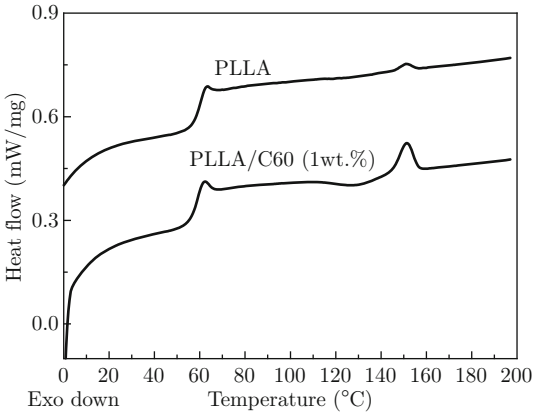

Fig. 3 The DSC 2nd heating curves of (a) neat PLLA and (b) PLLA with 1wt% of C60, respectively.

Table 1 DSC results of the second heating process for neat PLLA and PLLA/C60(1wt%) composites

Samples	T_c(℃)[a]	T_m(℃)[b]	ΔH_c (J/g)[c]	ΔH_m (J/g)[d]	X_c(%)[e]
PLLA	–	151.2	–	0.70	0.75
PLLA/ C60(1wt%)	127.4	151.5	−5.61	6.61	7.06

[a] Crystallization temperature of PLLA. [b] Melting temperature of PLLA. [c] Cold crystallization enthalpy change of PLLA. [d] Melting enthalpy change of PLLA. [e] Relative crystallinity of PLLA.

Assembling mechanism of C60 in PLLA matrix

Possible assembling mechanism of C60 needles in PLLA matrix was proposed as follows. With the evaporation of H_2CCl_2, the C60 solution became supersaturated, precipitated C60 would crystallize and combine with each other via Van der Waals force. Meanwhile, the molecules of PLLA would condense and crystallize slowly, some C60 could act an effective nucleating agent during solvent evaporation while H_2CCl_2[12] was used as the common solvent for both C60 and PLLA. As indicated by the aforesaid DSC analysis, PLLA could easily crystallize under the nucleating action of C60. The ordered alignment of PLLA molecular chain during crystallization could, in turn, promote the rest of C60 to migrate into the amorphous area or crystal boundary area of PLLA matrix. It is very likely that the C60 needle be assembled by the enriched C60 along PLLA crystal boundaries via Van der Waals force.

Conclusion

Needle-like C60 assembling has been obtained in preparing PLLA/C60 composites. The morphology of

the C60 needle studied by optical microscope and scanning electron microscope (SEM) show that the amount of C60 in the mixing system have some influences on the length of C60 needles. The largest C60 needles could have a diameter of 50 μm and a length of 1.6 mm. The energy dispersive spectra (EDS) analysis indicated the C60 needle was mainly composed of C60, DSC analysis indicated C60 accelerated the crystallization and lift the relative crystallinity of PLLA matrix. The results indicate the addition of PLLA influence the assembling behavior of C60. On the one hand, with the evaporation of H_2CCl_2, C60 precipitated from solution would crystallize and combine with each other via Van der Waals force. On the other hand, PLLA crystallize easily under the nucleating action of C60, the orderly movement of PLLA molecules would drive C60 to migrate into amorphous area and crystal boundary area, the C60 located in the crystal boundary area of PLLA matrix might tend to assemble into C60 needles via Van der Waals force. The assembly of C60 in other semicrystalline polymer matrix will be investigated in our future work.

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References

[1] T. Nakanishi, W. Schmitt, T. Michinobu, D. G. Kurthac and K. Ariga, Chem. Commun. 15, 5982 (2005). http://dx.doi.org/10.1039/b512320h

[2] H. Ji, J. Hu, L. Wan, Q. Tang and W. Hu, J. Mater. Chem. 18, 328 (2008). http://dx.doi.org/10.1039/b712696d

[3] J. Geng, W. Zhou, P. Skelton, W. Yue, I. A. Kinloch, A. H. Windle and B. F. G. Johnson, J. Am. Chem. Soc. 130, 2527 (2008). http://dx.doi.org/10.1021/ja076392s

[4] T. Tsuchiya, R. Kumashiro, K. Tanigaki, Y. Matsunaga, M. O, Ishitsuka, T. Wakahara, Y. Maeda, Y. Takano, M. Aoyagi,T. Akasaka, M. T. H. Liu, T. Kato, K. Suenaga, J. S. Jeong, S. Iijima, F. Kimura, T. Kimura and S. Nagaser, J. Am. Chem. Soc. 130, 450 (2008). http://dx.doi.org/10.1021/ja710396n

[5] C. H. Tan, P. Ravi, S. Dai, K. C. Tam and L. H. Gan, Langmuir 20, 9882 (2004). http://dx.doi.org/10.1021/la049747j

[6] X. Wang, S. H. Goh, Z. H. Lu, S. Y. Lee and C. Wu, Macromolecules 32, 2786 (1999). http://dx.doi.org/10.1021/ma981771e

[7] J. Yang, L. Li and C. Wang, Macromolecules 36, 6060 (2003). http://dx.doi.org/10.1021/ma025909b

[8] P. Ravi, S. Dai, C. Wang and K. C. Tam, J. Nanosci. Nanotech. 7, 1176 (2007). http://dx.doi.org/10.1166/jnn.2007.456

[9] Bruno Schmaltz, Martin Brinkmann and Claude Mathis, Macromolecules 37, 9056 (2004). http://dx.doi.org/10.1021/ma048421e

[10] W. Liu, R. Liu, W. Wang, W. Li, W. Liu, K. Zheng, L. Ma,Y. Tian, Z. Bo and Y. Huang, J. Phys. Chem. C 113, 11385 (2009). http://dx.doi.org/10.1021/jp900042h

[11] H. Tsuji, H. Takai, N. Fukuda and H. Takikawa, Macromol. Mater. Eng. 291, 325 (2006). http://dx.doi.org/10.1002/mame.200500371

[12] H. Tsuji, Y. Kawashima and H. Takikawa, J. Polymer Sci. Part B: Polymer Phys. 45, 2167 (2007). http://dx.doi.org/10.1002/polb.21215