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Structure and Properties of Biodegradable Polymer-Based Blends

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Summary: We have recently investigated the structure and properties of biodegradable polymer based blends. The biodegradable polymers studied in our work include poly(3-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-hydroxyvalerate) (PHBV), poly(butylene succinate) (PBSU), poly(ethylene succinate) (PES) and poly(ε-caprolactone) (PCL). The miscibility, morphology, crystallization and melting behaviour of biodegradable polymer based blends have been studied extensively, which were reviewed briefly in this manuscript.

Keywords: biodegradable; blends; crystallization; miscibility; morphology

Introduction

Biodegradable polymers have received considerable attention in the last two decades due to their potential applications in the fields related to human life such as environmental protection and ecology. According to the difference in the preparation methods, biodegradable polymers can be classified into two types. One is the biosynthetic polymers, such as bacterial polyhydroxyalkanoates (PHAs). Among them, PHB and PHBV are probably the most extensively studied biodegradable thermoplastic polymers. The other type is the chemosynthetic polymers such as aliphatic polyesters. PBSU, PES and PCL are three of them.

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In order to improve the properties and extend the application fields of the biodegradable polymers, polymer blending is an effective and convenient way. [1-15] In this manuscript, we briefly reviewed our recent research on the miscibility, morphology, crystallization and melting behaviour of polymer blends based on the five biodegradable polymers mentioned above. [8-15]

Miscibility of polymer blends can be divided into three types: namely, completely miscible, partially miscible and completely immiscible. Furthermore, in terms of the crystallizability of the components binary polymer blends can be classified into three types: namely amorphous/amorphous, amorphous/crystalline and crystalline/crystalline polymer blends. Blends in which both components are crystalline polymers have received much less attention than fully amorphous or amorphous/crystalline systems. Only a small number of works have been reported on the miscible polymer blends of two crystalline polymers with different chemical structures till now. However, they may be of considerable technological interest and offer the possibility of investigating crystallization and morphological behavior related to blend miscibility. On the other hand, it is also possible to determine how the crystallinity of one component affects the morphology, crystallization process, and properties of the other in the case of binary immiscible blends of two crystalline polymers.

We have recently done some research on the misciblity and crystallization behaviour in biodegradable polymer based blends. They include miscible crystalline/crystalline polymer blends, immiscible crystalline/crystalline polymer blends and miscible crystalline/amorphous polymer blends.

Miscible Crystalline/Crystalline Polymer Blends

PES/poly(ethylene oxide) (PEO) and PBSU/PEO blends are two new ideal models of binary miscible blends of two crystalline polymers. [8, 10-11]

PES/PEO blends were preapred with mutual solvent chloroform. PES and PEO were miscible blends of two crystalline polymers, which were crystallized at 50 °C to study the possibility of simultaneous crystallization of the two components by optical microscopy (OM). It was found that down to PES/PEO = 40/60 PES crystallized first and filled the whole space before PEO could nucleate. However, for PES/PEO =20/80, PES and PEO crystallized simultaneously and the formation of interpenetrated spherulites of PES by PEO was observed. It was proposed that the density of lamellae in PES spherulites was lower than that in PEO spherulites, and PEO spherulites continued to penetrate into PES spherulites on contact. [8]

Interpenetrated spherulites are occasionally formed in few miscible pairs of two crystalline polymers. Spherulites of one component continue to grow in the spherulites of the other component after they contact with each other. In our previous work, we reported the interpenetrated spherulites formation process of poly (butylene succinate) (PBSU)/poly (vinylidene chloride-*co*-vinyl chloride) (PVDCVC) blends and poly(ester carbonate) (PEC)/poly(L-lactic acid) (PLLA).[3-7] From the previous studies, we propose that the important factors in realizing interpenetrated spherulites are the difference in the lamella population density in the different spherulites of the two components, the sufficient amount of the melt of one component inside the spherulites of the other component, and the simultaneous spherulitic growth of both components.

As shown in Figure 1, PES and PEO crystallized simultaneously with PEO spherulite generally growing faster than PES spherulite. Instead of growth being arrested, the PEO spherulite continued to crystallize inside the PES spherulite and the growth front of the PEO type spherulite became distorted when it reached the PES type spherulite. Meanwhile, the brightness increased in the part of PES spherulite where the crystallization of PEO had occurred, and did not change where the crystallization of PEO had not occurred. These results indicated that PES spherulite was penetrated by PEO spherulite. However, it can also be observed that the outline of the brighter area is not consistent with the shape of the rest of the PEO spherulite, and the brighter area seems too large. It can be reasoned that the PEO fibrils grew faster inside the PES spherulite because the PEO content in the amorphous regions of the PES spherulite would be expected to be higher than the nominal melt concentration due to rejection of PEO from PES crystals. On the other hand, the PES spherulites stopped advancing towards the PEO spherulites.

PBSU/PEO blends were prepared with mutual solvent chloroform. The misciblity and crystallization behaviour were studied by DSC and OM. Experimental results indicate that PBSU is miscible with PEO as shown by the existence of single composition dependent glass transition temperature over the entire composition range. In addition, the polymer-polymer interaction parameter, obtained from the melting depression of the high-T_m component PBSU using the Flory-Huggins equation, is composition dependent, and its value is always negative. This indicates that PBSU/PEO blends are thermodynamically miscible in the melt. The morphological study of the isothermal crystallization at 95 °C (where only PBSU crystallized) showed the similar crystallization behavior as in amorphous/crystalline blends. Much more attention has been paid to the crystallization and morphology of the low-T_m component PEO. The two components crystallized sequentially not simultaneously when the blends were quenched from the melt directly to 50°C (one-step crystallization), and the PEO spherulites crystallized within the matrix of the crystals of the preexisted PBSU phase. Figure 2 shows the bright PEO spherulites growing in the matrix of the PBSU spherulites, which formed during the quenching process from the crystal-free melt to the crystallization temperature 50 °C. Before the temperature reached 50 °C, PBSU spherulites appeared and filled the whole space. Bright PEO spherulites thus nucleated and grew in the matrix of the PBSU spherulites after the crystallization temperature 50 °C was reached, which was lower than the melting point of PEO. [10]

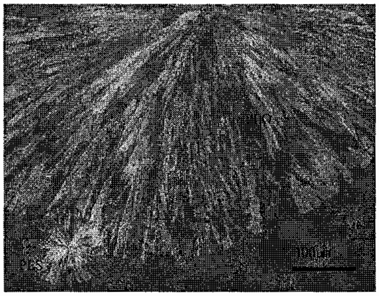

Figure 1. Formation of interpenetrated spherulites for PES/PEO=20/80 blend crystallized at 50 °C.

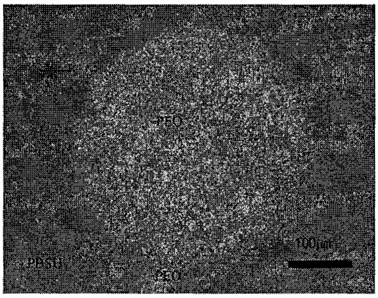

Figure 2. Bright PEO spherulites growing in the matrix of previously formed PBSU spherulites.

Immiscible Crystalline/Crystalline Polymer Blends

We also studied some binary immiscible blends of two crystalline polymers, including PHB/PBSU, PEO/PCL, PHBV/PCL and PBSU/PCL blends. The crystallinity of one component has a significant effect on the crystallization of the other.

PHB/PBSU blends, both biodegradable semicrystalline polyesters, were prepared with the ratio of PHB/PBSU ranging from 80/20 to 20/80 by co-dissolving the two polyesters in N, N-dimethylformamide and casting the mixture. Experimental results indicated that PHB showed some limited miscibility with PBSU for PHB/PBSU 20/80 blend as evidenced by the small change of the glass transition temperature and the depression of the equilibrium melting point temperature of the high melting point component PHB. However, PHB showed immiscibility with PBSU for the other three blends as shown by the existence of unchanged composition independent glass transition temperature and the biphasic melt. Nonisothermal crystallization of PHB/PBSU blends was investigated by DSC using various cooling rates from 2.5 to 10 °C/min. During the nonisothermal crystallization, despite the cooling rates used two crystallization peak temperatures were found for PHB/PBSU 40/60 and 60/40 blends, corresponding to the crystallization of PHB and PBSU, respectively, whereas only one crystallization peak temperature was observed for PHB/PBSU 80/20 and 20/80 blends. However, it was found that after the nonisothermal crystallization the crystals of PHB and PBSU actually coexisted in PHB/PBSU 80/20 and 20/80 blends from the two melting endotherms observed in the subsequent DSC melting traces, corresponding to the melting of PHB and PBSU crystals, respectively. The subsequent melting behaviour was also studied after the nonisothermal crystallization. In some cases, double melting behaviour was found for both PHB and PBSU, which was influenced by the cooling rates used and the blend composition.[9]

PEO/PCL blends were prepared by co-dissolving the two polyesters in chloroform and casting the mixture. Phase contrast microscopy was used to probe the miscibility of PEOB/PCL blends. PEO was immiscible with PCL because the melt was biphasic. Crystallization of PEO/PCL blends was studied by DSC and analyzed by the Avrami equation. The crystallization rate of PEO decreased with the increase of PCL in the blends while the crystallization mechanism did not change. In the case of the isothermal crystallization of PCL, the crystallization mechanism did not change, and the change in the crystallization rate was not very big, or almost constant with the addition of

PEO, compared with the change of the crystallization rate of PEO. [12]

PHBV/PBSU blends, both biodegradable semicrystalline polyesters, were prepared by co-dissolving the two polyesters in chloroform and casting the mixture. DSC and OM were used to study the miscibility and crystallization behaviour of PHBV/PBSU blends. PHBV is immiscible with PBSU as shown by the almost unchanged glass transition temperature and the biphasic melt. Crystallization of PHBV/PBSU blends was studied by DSC using two-step crystallization and analyzed by the Avrami equation. The crystallization rate of PHBV decreases with the increase of PBSU in the blends while the crystallization mechanism does not change. In the case of the isothermal crystallization of PBSU, the crystallization mechanism does not change. The crystallization rate of PBSU in the blends is lower than that of neat PBSU; however, the change in the crystallization rate of PBSU was not so big in the blends. The different content of the PHBV in the blends does not make a significant difference in the crystallization rate of PBSU. [13]

PBSU/PCL blends, both biodegradable chemosynthetic semicrystalline polyesters, were prepared with the ratio of PBSU/PCL ranging from 80/20 to 20/80 by co-dissolving the two polyesters in chloroform and casting the mixture. The miscibility and crystallization behaviour of PBSU/PCL blends were investigated by DSC and OM. [14]

PBSU was immiscible with PCL as evidenced by the composition independent glass transition temperature and the biphasic melt. Figure 3 shows the DSC traces of PBSU/PCL blends after melt quenching at a heating rate of 20°C/min. In the PBSU/PCL blends, a T_g at around -36 °C, which is close to that of neat PBSU, can be found for 80/20 and 60/40 blends, while the glass transition corresponding to PCL is not so apparent that it can not be determined accurately for 80/20 and 60/40 blends. On the other hand, a T_g at around -65 °C, which is close to that of neat PCL, can be found for 40/60 and 20/80 blends, while the glass transition corresponding to that of PBSU can not be found since it is masked by the cold crystallization peak temperature of PCL. The cold crystallization peak temperature of PBSU in the blends is found to shift to around -10 °C from around -5 °C for neat PBSU and is almost composition-independent, indicating that the cold crystallization of PBSU in the PBSU/PCL blends is enhanced by the addition of PCL. The cold crystallization peak temperature of PCL is found to remain around -54 °C for both the neat and the blended PCL. The decrease of the T_m of PBSU in the blends is no more than 3 °C. The T_m of PCL remains also unchanged in the blends. All the results mentioned above lead us to the conclusion that PBSU is immiscible with PCL in the blends.

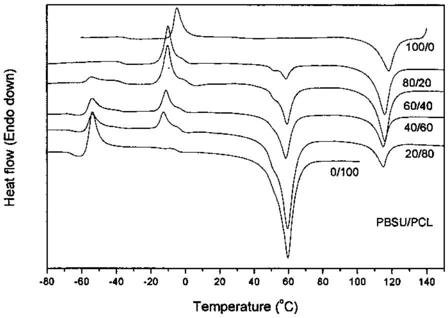

Figure 3. DSC traces of PBSU/PCL blends after melt quenching at a heating rate of 20°C/min.

However, during the crystallization from the melt at a given cooling rate, the crystallization peak temperature of PBSU in the blends decreased slightly with the increase of PCL, while that of PCL in the blends first increased and then decreased with the increase of PBSU. Moreover, both the crystallization peak temperature of PBSU and PCL shifted to the low temperature range with the increase of the cooling rate for a given blend composition. Double melting peaks or one main melting peak with a shoulder were found for both PBSU and PCL after the complete crystallization cooling from the melt, and were ascribed to the melting-recrystallization mechanism. It was found that the subsequent melting behaviour of PBSU/PCL blends was influenced apparently by the blend composition and the cooling rate used.

Miscible Crystalline/Amorphous Polymer Blends

PBSU/PVPh blends are a model of binary miscible crystalline/amorphous polymer blends, which were prepared with mutual solvent N, N-dimethylformamide. Miscibility has been investigated in blends of PBSU and PVPh by DSC. PBSU is miscible with PVPh as shown by the existence of single composition dependent glass transition temperature over the entire composition range. Shown in Figure 4 are the phase behaviour of PBSU/PVPh blends as a function of PVPh weight fraction. Figure 4 summarizes the composition dependence of T_g of the PBSU/PVPh blends. Meanwhile, the composition dependence of the cold crystallization temperature of PBSU and that of the T_m of PBSU are also shown in Figure 4. From Figure 4, it can be concluded that PBSU shows miscibility with PVPh from the composition dependence of T_g of the blends, the depression of the T_m of PBSU and the increase of the cold crystallization temperature of PBSU with increase in the PVPh content. In addition, the polymer-polymer interaction parameter, obtained from the melting depression of PBSU using the Nishi-Wang equation, is composition dependent, and its value is always negative. This indicates that PBSU/PVPh blends are thermodynamically miscible in the melt. [15]

Preliminary morphology study of PBSU/PVPh blends was also studied by OM. OM experiments show the spherulites of PBSU become larger with the PVPh content, indicative of a decrease in the nucleation density, and the coarseness of PBSU spherulites increases too with increasing the PVPh content in the blends. The miscibility of PBSU/PVPh blends may be due to the formation of hydrogen bonding between the carbonyl group of PBSU with the hydroxyl group of PVPh.

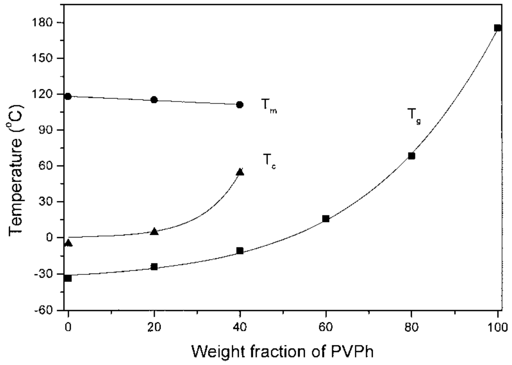

Figure 4. Phase behaviour of PBSU/PVPh blends as a fuction of PVPh weight fraction.

Conclusion

We briefly reviewed our recent research on the structure and properties of biodegradable polymer based blends. It could be concluded that the structure and properties of biodegradable polymer based blends were influenced significantly by the miscibility, phase behaviour and crystallization conditions. In conclusion, it is of great interest to study the structure and properties of biodegradable polymer based blends from both the academic and the industrial viewpoints.

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