Blending and Characterizations of Microbial Poly(3-hydroxybutyrate) with Dendrimers

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ABSTRACT: Blending of microbial polyester poly(3-hydroxybutyrate) (PHB) with various dendritic polyester oligomers or dendrimers was achieved by solution casting to improve the film forming ability of PHB. Films of the blends were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron micrograph (SEM), and Fourier transform infrared spectroscopy (FTIR). It was revealed that there were mainly two types of interactions in the blending system: the plasticizing or lubricating effect of the low melting spherical dendrimers molecules improved the polymer chain mobility through the suppression of PHB crystallization in the blends; The dendrimers also functioned as crosslinking agents or antiplasticizing agents via weak hydrogen bonding to enhance the overall intermolecular interactions which decrease the chain mobility and thus cause the increase of glass transition temperature (T_g) of PHB. TGA results concluded that incorporating the dendrimers could retard the thermal decomposition of PHB and enhanced its thermal stability accordingly. With the above blend processes, the so-obtained PHB possessed better film forming ability and even patterned surface structures. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3782–3790, 2006

Key words: poly(3-hydroxybutyrate); dendrimers; polyesters; blending; crystallinity

INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) is one of the typical natural biopolyesters produced by many microorganisms as intracellular carbon and energy storage compounds.[1–3] However, PHB has several inherent deficiencies for use as a practical polymer materials, such as its brittleness due to its high crystallinity and thermal instability near its melting point of 180°C.[4,5] To overcome the drawbacks of PHB and obtain some useful new material properties, physical blending and chemical modification have been adopted.[6–9] There are many attempts to blend PHB with other flexible polymers or low molecular weight plasticizers to turn PHB into a materials with improved properties in impact strength, film formation, processing, mechanical strength, amphiphilicity, biodegradability, and biocompatibility.[10–13] Previous investigators revealed that PHB is miscible with poly(ethylene oxide),[14] poly(vinylidene fluoride),[4] poly(vinyl acetate),[1] poly(epichlorohydrin),[15] poly(methyl methacrylate)[16,17] and poly(cyclohexyl methacrylate).[16] PHB prepared via bacterial fermentation is partially miscible with ethylene–propylene rubber,[1] ethylene-vinyl acetate copolymer,[18] poly(vinyl phenol)[19,20] poly(vinyl alcohol),[21,22] poly(L-lactide),[23,24] poly(caprolactone)[25,26] and also the chemically synthetic poly(3-hydroxybutyrate).[27,28]

Dendrimers and hyperbranched polymers have attracted more and more interest since mid 1980s, and recent studies have focused on blends of dendrimers and hyperbranched polymers with linear polymers.[29,30] Owing to the unique structures of the dendrimers and hyperbranched polymers, such as high peripheral functionality, spherical structures, blending of linear polymers with dendrimers and hyperbranched polymers would endow the materials with novel properties and create new class of materials.

Kim and Webster[31] reported low melting viscosity and improved thermal stability of polystyrene (PS) with the addition of hyperbranched polyphenylenes. Massa et al.[32] reported increasing tensile strength and compressive modulus together with decreasing strain to break and toughness in aromatic hyperbranched polyester/bisphenol A PC blends compared with pure polycarbonate (PC). Studies were conducted by Carr et al.[33] on 5, 10, and 20% miscible blends of two aryl ester dendrimers with poly(ethylene terephthalate) (PET); the smaller dendrimers acted as a plasticizer in that it reduced PET chain interactions, resulting in a slow decrease in the glass-transition temperature (T_g) with increasing dendrimer content. The larger, highly branched dendrimer acted as an antiplasticizer; it

increased chain entanglement density caused by dendrimer-chain interaction and resulted in a slight increase in T_g with increased dendrimer content. This antiplasticizing effect decreased with incorporation of smaller, less structurally complex dendrimers.[33]

Many studies[34] showed that the blending of hyperbranched structures or dendrimers with linear polymers is a promising route to prepared novel materials. Blending linear polymers with low concentration of dendrimers may enhance the physical properties of the linear polymers.

The purpose of our investigation was to seek the possibility of improving the PHB processibility and mechanical properties via the addition of dendrimers. To our knowledge, this is the first time that dendrimers were used for improving PHB properties.

EXPERIMENTAL

Materials

Bacterial poly(3-hydroxybutyrate) (PHB) in white powder was kindly provided by Jiangsu NanTian (China). The PHB was used without further purification. Its weight and number–average molecular weights are $M_w = 8.3 \times 10^5$ and $M_n = 3.3 \times 10^5$, respectively, estimated by gel-permeation chromatography (GPC) with chloroform as the eluent at 30°C. Two dendrimers (dendritic alkyl polyester oligomers) were well used for the blending. Dendrimer F4308 (total molecular weight 5800) with a four dendron polyester oligomer core of molecular weight 3500 consisting of eight peripheral C18 hydrocarbon chains and 24 peripheral hydroxyl end groups, and Dendrimer F3312 (total molecular weight 5800) with a three dendron polyester oligomer core of molecular weight 2500 consisting of 12 peripheral C18 hydrocarbon chains and 12 peripheral hydroxyl end groups, were supplied by Shantou Polymer Additives (China). The M_w and M_n of F4308 are 3000 and 2500, respectively, and of F3312 are 3200 and 2700, respectively, based on GPC estima-

tion. The smaller values of the molecular weights by GPC may be induced from the spherical shape of the dendrimer molecules. The F4308 possesses a more compact structure than F3312 does (Fig. 1).

Preparation of samples

All film samples were prepared by a solution casting technique using chloroform as a solvent.[35] The detailed procedure is described here: a certain amount of dendrimer was dissolved completely in chloroform (CHCl$_3$), followed by the addition of PHB powder to the above-prepared dendrimer solution; the mixture was stirred to form a homogenized and clear solution of dendrimer with PHB. The solution was thus cast onto a petri dish and allowed to evaporate under room temperature for removal of the solvent. Finally, the formed films were dried *in vacuo* at 40°C for 24 h to completely eliminate the solvent and films were stored in a desiccator.[35] Various blending ratios of PHB/dendrimers were prepared, with weight ratios of PHB/dendrimer ranging from 80/20 to 40/60.

Characterization of PHB/dendrimer blends

Differential scanning calorimetry analysis

Differential Scanning Calorimetry (DSC) thermograms were recorded on a Q-100 DSC instrument (TA instrument, USA) calibrated with indium. Samples of cast films weighted 5 mg were packed in an aluminum pan and then heated from −60°C to 200°C at a scanning rate of 10°C/min (first run). The melting temperature (T_m) and melting enthalpy (ΔH_f) were determined from DSC endothermal peaks. After 1 min annealing, the sample was cooled to −60°C, annealed for 1 min, and then reheated to 200°C at a scanning rate of 10°C/min (second run). The glass transition temperature (T_g) was obtained from the second heating run. In the presence of multiple endothermal peaks, the maximum peak temperature was taken as T_m (Fig. 2).
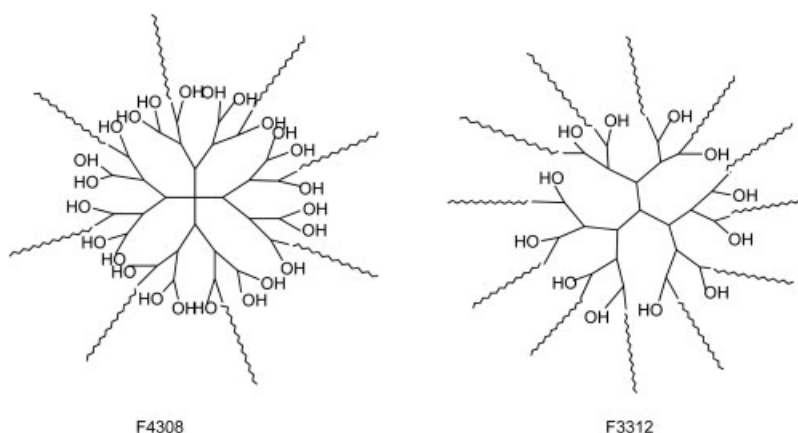

F4308   F3312

Figure 1 A schematic structure illustration of dendritic alkyl polyester Dendrimer F4308 and F3312.
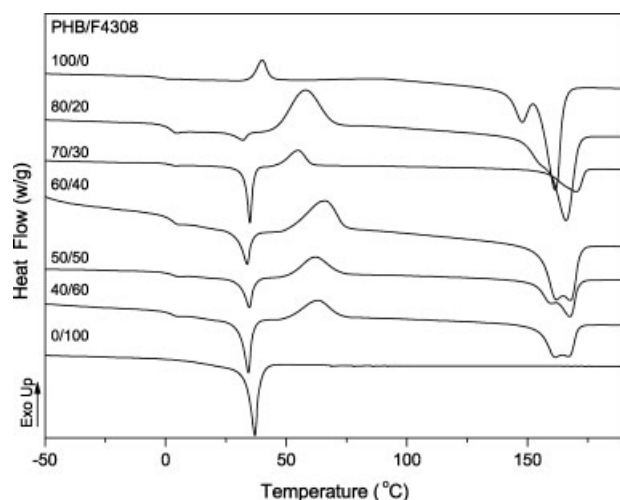
Figure 2 DSC thermograms of PHB and dendrimer blends (second heating run). Samples of cast films weighted about 5 mg were packed in an aluminum pan and then heated from $-60°C$ to $200°C$ at a scanning rate of $10°C/min$.

Thermogravimetric analysis

Thermogravimetry analysis (TGA) was performed on a Q-50 instrument (TA Instrument, USA) calibrated with indium. The temperature was ramped at a heating rate of $10°C/min$ under nitrogen, to a temperature well above the degradation temperature of the polymers ($600°C$).

Scanning electron microscope

A JEOL JSM-6360 LA (JEOL, Japan) scanning electron microscope (SEM) was used to study the morphology of the blend samples. Cross section samples for SEM observation were prepared by sample fracturing immediately after they were frozen in $-80°C$ refrigerators. Surface images were recorded at a voltage of 10 kV; before observation, they were coated with a thin conductive layer of gold.

FTIR measurement

FTIR spectra of polymer films were recorded on a Nicolet Magana 750 FTIR spectrometer (Nicolet, USA) by transmission method at room temperature in the range from 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1}. The films of the samples were cast from the $CHCl_3$ solution onto KBr pellets. The films were dried at room temperature until $CHCl_3$ was completely removed.

RESULTS AND DISCUSSION

A schematic illustration of the dendrimers is shown in Figure 1. The dendrimers with different numbers of surface hydroxyl groups were blended with PHB. When the surface peripheral end groups are totally hydroxyl groups, the dendrimers have very limited solubility in chloroform. No sufficient blending between PHB and the dendrimers could be made (Table I). However, when all the 32 surface groups are substituted with C18 hydrocarbon chain, the dendrimers would be too hydrophobic to separate from the PHB phase and no appropriate blending could be made either (Table I). When the dendrimers contain 24 hydroxyl groups and eight C18 hydrocarbon chains on the periphery in the case of dendrimer F4308, or 12 hydroxy groups and 12 C18 hydrocarbon on the periphery in the case of dendrimer F3312, they showed an appropriate hydrophobicity, and thus had good solubility in chloroform, homogeneous blends of PHB and dendrimers could be prepared. Therefore, the dendrimers with above surface groups were used for blending with PHB.

PHB consisting of carbonyl group in the backbone is a biopolyester. The dendrimers containing both hydroxyl groups and hydrocarbon chains on the surface and a polyester oligomer core should be miscible with PHB. The blending of PHB and the dendrimers may be able to form hydrogen bonding via the interaction of the carbonyl groups in PHB and the hydroxyl groups in the dendrimers. The surface hydrocarbon chains could be used to adjust the hydrophobicity for a better compatibility performance. Thus, the flexibility, hydrophilicity, and compatibility of the PHB blends would be improved.

Thermal behavior

Blends of PHB and the dendrimers at different ratios were achieved via solution casting from chloroform.

TABLE I
Dendrimers Used for the PHB Blending

Dendrimer	Peripheral hydroxyl groups	Peripheral C18 hydrocarbon chain	Solubility in $CHCl_3$	Blending with PHB
F4300	32	0	Not soluble	Immiscible
F4332	0	32	Soluble	Phase separation
F4308	24	8	Soluble	Miscible
F3312	12	12	Soluble	Miscible

PHB and dendrimers were blended by a solution casting technique using chloroform as a solvent.[35]

TABLE II
T_m, ΔH_f, and X_c% values of PHB/F4308 Blends

PHB% (w/w)	First Run			Second Run		
	T_m (°C)	ΔH_f (J/g)	X_{c1} (%)	T_m (°C)	ΔH_f (J/g)	X_{c2} (%)
100	173.2	82.9	56.8	161.5	81.3	55.7
80	172.7	80.0	68.5	165.9	73.4	62.8
70	167.5	55.6	54.4	170.2	38.3	37.5
60	169.4	58.7	67.0	167.7	57.8	66.0
50	170.7	37.8	51.8	167.5	33.9	46.5
40	168.7	37.1	63.5	167.6	32.4	55.4

5 mg samples were packed in an aluminium pan and then heated from −60°C to 200°C at a scanning rate of 10°C/min (first run). After 1 min annealing, the sample was cooled to −60°C, annealed for 1 min, and then reheated to 200°C at a scanning rate of 10°C/min (second run).

The DSC thermograms of the blends are shown in Figure 2. The dendrimers have a melting point of 35–36°C. The pure PHB polyester, however showed two endothermal peaks in between 140 and 200°C, the peak at the higher temperature located at 173.2°C is attributed to the melting of the crystalline film. Another endothermal peak appearing at a lower temperature is also clearly shown at around 142.5°C which is probably due to the melting of the imperfect crystals formed during the sample preparation. The melting enthalpy (ΔH_f) was obtained from the area of the two endothermal peaks. The crystallinity degree (X_c) was calculated based on the melting enthalpy of 146 J/g of 100% PHB crystalline.[36] The DSC data of the blends are summarized in Table II.

Compared with pure PHB, an intensified cold crystallization of all the blend samples at about 65°C (Fig. 2) may be the results from the inability of all of the crystallizable chains to crystallize completely during the cooling cycles. The remaining of dendrimer single melting peaks at 36°C in all the blends indicates that the dendrimer is free to form the crystal and still kept its crystal intact. The dendrimer crystallization is induced from the C18 hydrocarbon chains on the surface. The crystal intact dendrimer with low melting point would function as a lubricant or plasticizer to increase the mobility of the PHB chains. This is different from the case of small molecules which was dispersed in the blends and no crystallization of the small molecules could occur.[35]

T_m in the first heating of PHB/F4308 blends was slightly decreased when the PHB content increased, yet the T_m of the second heating run was increased obviously. It is easy to understand as stated earlier that blending of the dendrimers with low melting point would have a lubricating or plasticizing effect and cause the decrease of PHB melting point. This was clearly manifested in the first heating run (Table II). In the second heating run, the dendritic polyesters functioned as a lubricant to enhance the chain mobility of

PHB, especially for the densely packed PHB microcrystal or ordered chain regions. With increasing dendrimers contents, the PHB microcrystals or ordered chains could be more easily moved to pack into a more dense or perfect crystalline structure as PHB is still a highly crystalline polymer with low crystallization rate. This effect was more profound during the cooling and reheating process, which lead the materials to crystallization. This would be the possible reason to possess higher T_m during the second DSC heating run (Fig. 2 and Table II). In the blend containing 70% PHB, the above discussed plasticizing effect became stronger, leading to a lower T_m in first heating run and a higher T_m in the second heating run. Results also revealed that the enthalpy of PHB fusion, ΔH_f decreased in a linear from 82.9 to 37.1 J/g in the first run and from 81.3 to 32.4 J/g in the second run (Table II). A lower melting enthalpy in the second run may be induced from lower crystallization degree even the crystal possesses better and more dense structure. As the crystallinity degree (X_c) of PHB crystalline phase can be calculated using the following equation:

$$X_c\% = 100 \times \Delta H_f[W_{\mathrm{PHB}}(\Delta H_f^0)]$$

where ΔH_f^0 (= 146 J/g)[36] is the thermodynamic melting enthalpy of a 100% crystalline PHB. ΔH_f is the apparent melting enthalpy corresponding to PHB crystallizable component, and W_{PHB} is the weight fraction of PHB in the blend.

The crystalline degrees of PHB in all the blends were maintained at between 50 and 60% with the exception of that containing 70% PHB (Table II). It seems that the addition of dendrimer F4308 did not affect the crystalline degree of PHB in most the cases. When PHB content was at 70%, lower ΔH_f and the lowest X_c (37.5%) of PHB were observed. This means that 70% PHB containing blend had the lower crystalline degree yet higher T_m, as discussed previously. This may be resulted from the better plasticizing effect which

TABLE III
T_m, ΔH_f, and X_c% of PHB/F3312 Blends

PHB% (w/w)	First Run			Second Run		
	T_m (°C)	ΔH_f (J/g)	X_{c1} (%)	T_m (°C)	ΔH_f (J/g)	X_{c2}%
100	173.2	82.9	56.8	161.5	81.3	55.7
80	172.6	71.2	61.0	169.6	64.6	55.3
70	170.3	44.9	43.9	168.8	41.0	40.1
60	173.3	42.0	47.9	170.2	39.0	44.5
50	173.4	38.0	52.1	170.3	33.8	46.3
40	173.2	30.1	51.5	170.0	29.2	50.0

5 mg samples were packed in an aluminium pan and then heated from −60°C to 200°C at a scanning rate of 10°C/min (first run). After 1 min annealing, the sample was cooled to −60°C, annealed for 1 min, and then reheated to 200°C at a scanning rate of 10°C/min (second run).
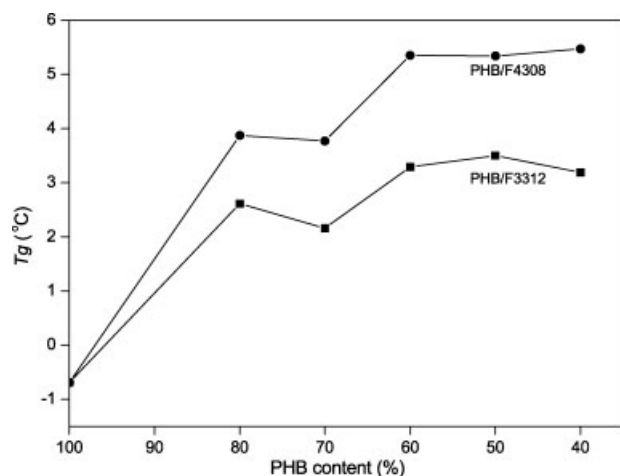
Figure 3 Glass transition temperature (T_g) of PHB and dendrimer blends.

depresses the crystallization of PHB and pushes the already formed microcrystals or ordered chains to pack into more perfect crystalline structures in the blend.

The melting temperature T_m of PHB in the blends of PHB/F3312 was varied slightly, the T_m in the second run was lower than the T_m in the first run (Table III), this trend was the same compared with PHB/F4308 blends (Table II). The ΔH_f decreased from 82.9 to 30.1 J/g or 81.3 to 29.2 J/g when PHB decreased from 100 to 40%. It was noted that the trend of decrease of PHB crystallinity (X_c) degree was obvious, but they were lower than the blends of PHB/F4308 at the same ratios. The possible explanation of this difference between F4308 and F3312 may be due to the molecular structure compactness. The chemical structure of F3312 is less compact than F4308 (Fig. 1). The less compact structure would enhance the molecular entanglement

and the molecular penetrating between dendrimer and PHB. This interaction would suppress the crystallization of PHB and result in the decrease of crystalline degree. Similar to dendrimer F4308, the 70% PHB with 30% F3312 gave the lowest crystalline degree.

There are two kinds of intermolecular interactions between PHB and the dendrimers. The dendrimers are actually kinds of oligomers (molecular weight 5800) with low melting point; they possess low melting viscosity and also act as plasticizers in the blending system. The plasticizing effect would enhance the movement of the molecular chains. On the other hand, carbonyl group on the PHB backbone is proton acceptor. The dendrimers have many hydroxyl groups on their surface and these hydroxyl groups can form intermolecular hydrogen bonding with PHB carbonyl groups. This would hinder the mobility of PHB molecular chains and function as an antiplasticizing agent. The net results of these two interactions would lead to plasticizing or antiplasticizing effect depend on which is stronger.

With increasing content of F4308 or F3312 in the blends, the T_g of PHB component increased from $-0.7°C$ to 5.5 or 3.2°C (Fig. 3). The increase of T_g reflects the antiplasticizing effect of the dendrimers in the amorphous regions of the PHB component. These changes of physical properties should be explained from the existence of the interaction between PHB and the dendrimers. A probable interaction is the hydrogen-bonding interaction between the carbonyl groups in the PHB chains and the hydroxyl groups on the dendrimer periphery. This seems to be consistent with the results in Table III. Because of the formation of the intermolecular hydrogen bonds, F4308 and F3312 might also act as a physically crosslinking agent in the blends, which would lower the flexibility of the
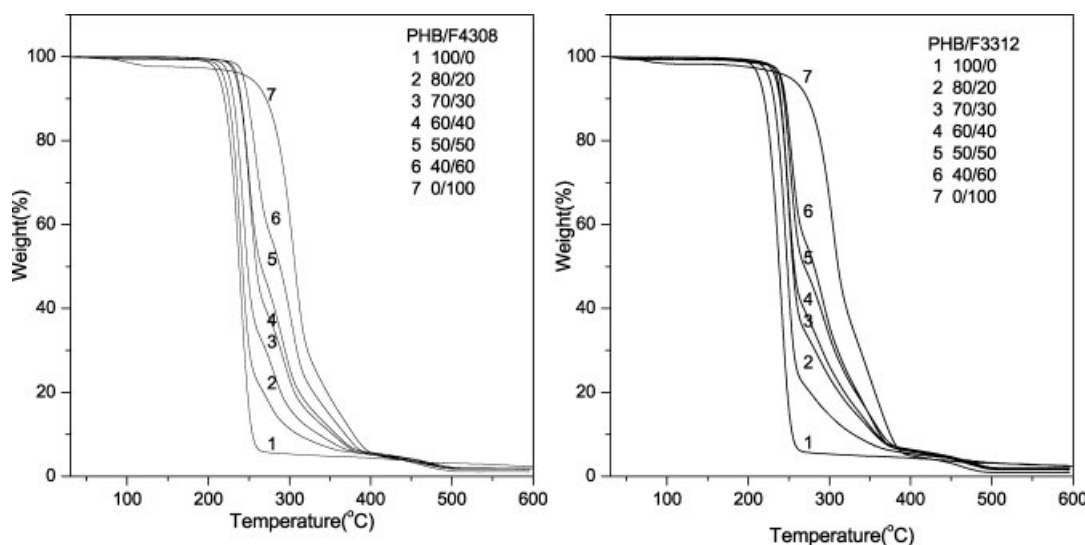

Figure 4 TGA curves of PHB/F4308 (a) and PHB/F3312 (b) blends. The temperature was ramped at a heating rate of 10°C/min under nitrogen, to a temperature well above the degradation temperature of the polymers (600°C).
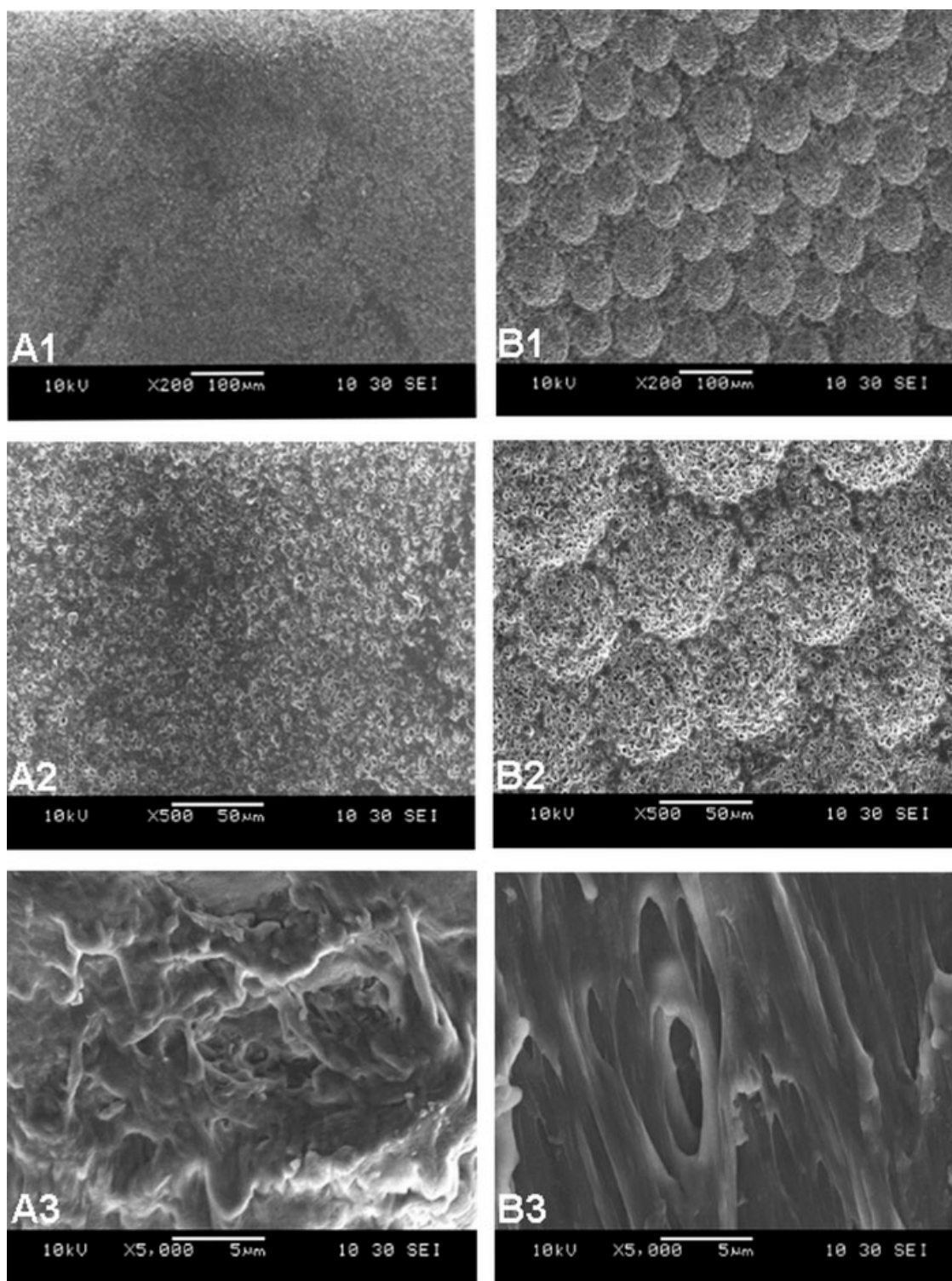
Figure 5 Scanning electron micrographs of the blend films of PHB and PHB/F4308 (70/30). A1: PHB surface; B1: PHB/F4308 surface; A2: PHB surface; B2: PHB/F4308 surface; A3: PHB cross section; B3: PHB/F4308 cross section. Surface images were coated with a thin conductive layer of gold. Cross section samples were prepared by sample fracturing immediately after they were frozen in −80°C refrigerators.

PHB chain, resulting in the increase of the T_g. This was also observed in the blending of dendrimer and PET by Carr et al.[33] Again at 70% PHB containing blend, a smaller T_g increase was detected and this might be

due to the stronger plasticizing effect and lower crystallization degree which caused the smaller increase of T_g in some way. Compared the two dendrimers F4308 and F3312, the less T_g increase from the presence of

dendrimer F3312 may be a result of the less compact and more flexible structures of this dendrimer.

Thermal stability

As the thermal instability is one of the main PHB drawbacks. The decomposition temperature of PHB is very close to its melting point. This makes the PHB very difficult to process. How to improve the processability of PHB is very important for the practical applications. Figure 4 shows the TGA curves of the PHB, dendrimer and their blends. The weight loss of pure PHB occurred in one step at the temperature exceeding 220°C. The thermal stability of the dendrimers was better than that of the pure PHB. The thermal decomposition temperature of the dendrimers at the T_p (peak temperature of the first derivative trace)[37] was all at approximately 305°C. However, the T_p of pure PHB was just at 240°C. The blending of PHB with the dendrimers significantly improved the thermal stability of the PHB, demonstrated by a decomposition temperature increase of 10 to 25°C. The thermal decomposition thus occurred at two stages. From the weight loss ratio, it can be observed that the decomposition of PHB component came first, followed by decomposition of the dendrimers. The enhanced thermal stability in the blending would improve the processing ability of PHB.

Morphology observation

SEM observations on the surface and fracture cross sections of PHB and PHB/Dendrimer F4308 are shown in Figure 5. The surface of pure PHB film was smooth even though it is quite brittle. It is quite interesting to observe that regularly patterned surface of hemispherical extrudes with diameter of approximately 50 μm was formed from the blend of 70% PHB plus 30% F4308. No such a regular patterned surface was found from other blend ratios. Combined with other determinations as discussed earlier, it can be found that the 70% PHB blend always showed some unique characteristics, which might be the demonstration of a stronger plasticizing interaction and more perfect PHB crystalline formed. This blend would lead to a more distinct phase separation and the patterned structure observed. The patterned surface should be very interesting to biomedical applications as it can guide the specific cell attachment, cell growth and proliferation. The fracture observation however revealed that the addition of dendrimers turned the brittle facture cross section to toughened fracture cross section with ductile and striped fracture surface [Fig. 5(A3) and 5(B3)]. The PHB polyester would be toughened via blending with the dendrimers. During our experiments, only brittle PHB films were formed without the presence of the dendrimers. Through the blending with dendrimers, flexible PHB film with smooth surface could be pre-

pared, especially in the case of 70% PHB containing blend, which formed the most flexible film. This confirms the stronger plasticizing effect of the blend.

FTIR analysis

Figure 6 shows the enlarged sections of FTIR spectra of PHB, the dendrimers and PHB/dendrimer blends. In the 3200–3600 cm^{-1} spectra region, PHB did not show any absorption due to the very few hydroxyl end group of the long molecular chains. The pure dendrimers showed a broad absorption between 3300 and 3600 cm^{-1} because of the rich hydroxyl groups located on the dendrimer periphery. When PHB was blended with the dendrimers, the blends gave a sharp and small absorption at 3435 cm^{-1}. The band at 3435 cm^{-1}, attributed to dendrimer hydroxyl end groups that have hydrogen bonding with the carbonyl group in PHB. The small peak may reveal the weak hydrogen bonding in the PHB/dendrimer blends. The region between 1720 and 1750 cm^{-1} contains absorption from PHB carbonyl group and carbonyl group of dendrimers which are dendritic polyesters. Compared with carbonyl bimodal absorptions at 1720 and 1750 cm^{-1} of pure PHB and dendrimers, it was noted that the blends showed a broad absorption shifted to the middle of these bimodals. This shift includes the change of the absorption at 1750 cm^{-1} to a lower wavenumber such as to 1730 cm^{-1}. This observation revealed that the hydrogen bonding really exists in the blends, even if it was weak in the system.[36] As the 1750 cm^{-1} is the carbonyl absorption of PHB in amorphous region, this shift also indicates that the hydrogen bonding interaction mainly exists in the amorphous region. That might be the reason of the increase of T_g of PHB as discussed previously. Again, compared the hydroxyl absorption regions of the two dendrimer blend systems, it was noted that the dendrimer F3312 with three dendrons possesses less compacted and more flexible structures, leading to stronger hydrogen bonding. Dendrimer F4308 with four dendrons is more compacted and less flexible, therefore, weaker hydrogen bonding was induced.

CONCLUSIONS

PHB properties were modified by blending with alkyl polyester dendrimers with molecular weight 5800. Flexible film was prepared through solution casting due to the plasticizing effect of the low melting dendrimer molecules. DSC and TGA results showed that the addition of the dendrimers causes not only increase of T_g in the amorphous region, but also the increase of crystal perfect and thus T_m. The blends improved the thermal stability of PHB component. There are weak intermolecular hydrogen bonds between the hydroxyl groups of the dendrimers and carbonyl groups of PHB. The hydrogen bonds result in increasing T_g of PHB
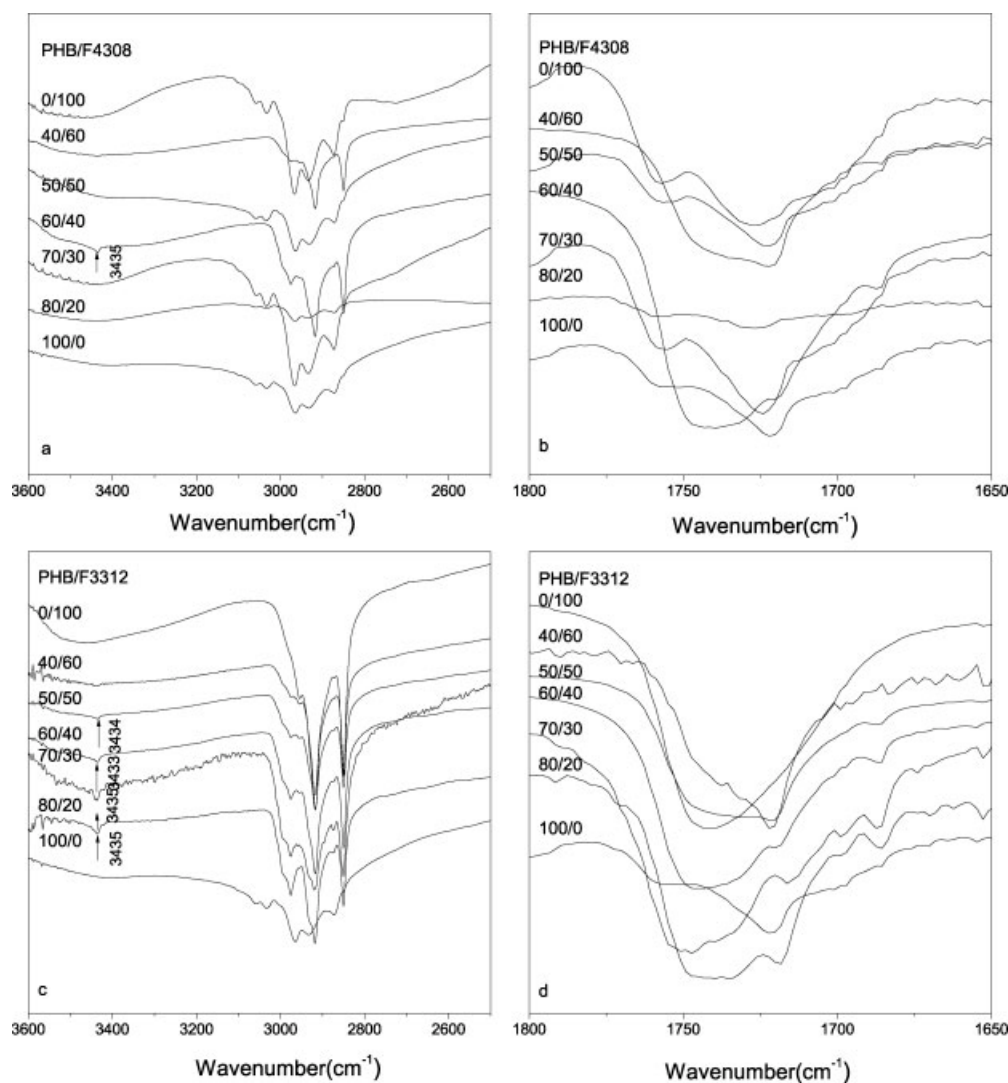
Figure 6 Enlarged sections of FTIR spectra of PHB, F4308, PHB/F4308 blends (a, b); PHB, F3312, and PHB/F3312 blends (c, d) in hydroxyl and carbonyl regions. Samples were cast from the CHCl₃ solution onto KBr pellets.

component in the blends. The interaction between PHB and dendrimer reduces the crystallization degree in the case of blending with less compact or more flexible dendrimer F3312. But blending with more compact dendrimer F4308 seems no strong effect on the crystalline degree.

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