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Miscibility and transesterification of phenoxy with biodegradable poly(3-hydroxybutyrate)

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The miscibility and transesterification of poly(hydroxyl ether of bisphenol A) (phenoxy) and poly(3-hydroxybutyrate) (PHB) were investigated by means of differential scanning calorimetry (DSC) and Fourier transform IR spectroscopy (*FT*i.r.). The blends, prepared by casting from a dimethylformamide solution at 80°C and drying in vacuum at 80°C, heated from room temperature to 180°C at a rate of 10°C min^{-1}, are miscible at 180°C when the PHB content is less than about 20 wt.% and almost immiscible when the PHB content is over 20 wt.%. The *FT*i.r. spectra reveal that the PHB content in the THF soluble fraction of the blends containing 30 wt.% PHB annealed at 180°C increases with increasing annealing time. Both the extraction and the *FT*i.r. experiments indicate that transesterification occurs between phenoxy and PHB. When the transesterification is complete, hence when the annealing time is long enough, a single phase is formed. During transesterification, the number of non-hydrogen-bonded OH groups of phenoxy first increases, passes through a maximum and then decreases with increasing annealing time at 180°C, becoming negligible once a single phase is formed. An explanation is proposed for this behavior. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: miscibility; transesterification; phenoxy)

INTRODUCTION

Considerable effort was made to study the miscibility and phase behavior of two polymers[1–3]. Polymer pairs with specific interactions, such as ion–ion[4], ion–dipole[5], acid–base[6], hydrogen-bonding[7], are often miscible. For condensation polymers, such as polyesters or polyamides, transreactions may occur during the melting process at high temperatures[8]. Depending upon the process conditions, the initial immiscible polymer pair can become partially and even completely miscible. Extensive research has been focused on some polyester pairs, such as polycarbonate (PC)/poly(ethylene terephthalate) (PET)[9], PC/poly(butylene terephthalate) (PBT)[10], polyarylate/liquid crystal polyester[11], phenoxy/PBT[12], etc. The transreactions include intermolecular alcoholysis, acidolysis and direct midchain ester exchange. All three reactions are generally called transesterification.

The natural poly(3-hydroxybutyrate) (PHB) is a biodegradable polyester produced by a number of bacteria as a reserve of carbon and energy[13–15]. Microbial PHB has an exceptional stereochemical regularity and its crystallinity is as high as 60%–90%[16]. This material is, however, brittle owing to the progressive crystallization upon ageing with the formation of large size spherulites[15]. PHB was found to be miscible with a few polymers such as poly(ethylene oxide)[17], poly(vinyl acetate)[18], poly(vinylidene fluoride)[19], poly(epichlorohydrin)[20], poly(ϵ-caprolactone)[21] and poly[(*R*,*S*)-lactide][22] and to have limited miscibility[23] or even complete miscibility[24,25] with poly(methyl methacrylate). The properties of PHB can be improved by copolymerization with other monomers such as hydroxyvaleric acid[26], caprolactone and lactide[27]. Being a polyester, PHB may form, in principle, via transesterification in the molten state, miscible blends with other mainchain polyesters such as PET, PBT, polyarylate or PC. Such a possibility is, however, greatly limited, since the melting points of these polymers are well above that of PHB and under such conditions PHB suffers severe degradation.

Phenoxy is a commercial thermoplastic polyether, whose secondary hydroxyl groups can be involved in hydrogen-bonding or alcoholysis with polyesters[12,28]. The alcoholysis occurs in milder conditions and much faster than the direct midchain ester exchange. It is appropriate to choose phenoxy as a partner to investigate the transreaction with PHB, since the alcoholysis can be carried out with reasonable speed at a relatively low temperature (only a little above the melting point of PHB) at which the thermal degradation of PHB is negligible. In this paper, it will be shown that some transesterification of phenoxy and PHB occurs even during the dissolution and casting stages of the preparation of the phenoxy/PHB blends, at temperatures well below the melting point of PHB. Single-phase blends were, however, obtained by annealing them for a sufficiently long time at 180°C because only then the transesterification became sufficiently advanced. Differential scanning calorimetry (DSC) and Fourier transform IR spectroscopy (*FT*i.r.) experiments allowed identification of the conditions under which the transesterification represents the mechanism of compatibilization of phenoxy and PHB.

EXPERIMENTAL DETAILS

Materials

Poly(3-hydroxybutyrate) (PHB, natural origin, Aldrich) and poly(hydroxyl ether of bisphenol A) (phenoxy) (Scientific Polym. Products) were used as received.

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Blend preparation

The blends were prepared by dissolving phenoxy and PHB in a common solvent, dimethylformamide (DMF), at 120°C, followed by casting at 80°C and finally by vacuum oven drying at 80°C.

Differential scanning calorimeter (DSC) characterization

The thermal behavior of the samples was examined using a Du Pont 910 differential scanning calorimeter under nitrogen. Two kinds of experiments have been performed. In the first kind, the samples were first heated up to 180°C, with a heating rate of $10^{\circ}C\ min^{-1}$, and held at 180°C for 1 min to remove any previous thermal history of the materials. Then the samples were rapidly quenched in liquid nitrogen. A second scanning was carried out from −40 to 180°C with a heating rate of $10^{\circ}C\ min^{-1}$. The data were collected during the second scanning. In the second kind of experiments, the samples were heated from room temperature to 180°C, annealed at 180°C for a certain time, then quenched in liquid nitrogen and reheated from −40 to 180°C with a heating rate of $10^{\circ}C\ min^{-1}$. This procedure was repeated several times with the same sample, at increasing annealing times. T_g was taken as the mid-point transition of the heat capacity; the cool crystallization temperature T_{cc} and melting temperature T_m were taken as those of the main exo- and endo-thermal peaks respectively.

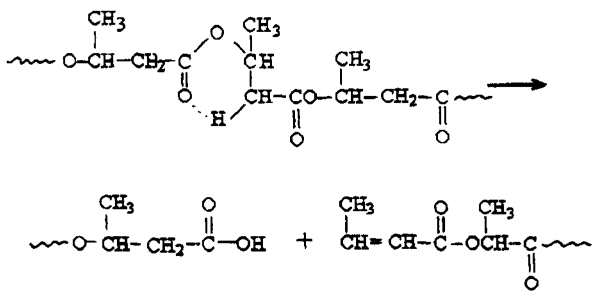
***FT*i.r. characterization**

Phenoxy/PHB blends containing 30 wt.% PHB were annealed at 180°C for 10 and 30 min respectively. The two specimens along with another specimen free of annealing were subjected to extraction with tetrahydrofuran (THF) for 10 h in a Soxhlet. THF is a good solvent for phenoxy but a poor solvent for PHB. The THF soluble fractions were concentrated and cast onto sodium chloride plates. The thin films were thoroughly dried in a vacuum oven at 60°C and the *FT*i.r. analysis was carried out using a Perkin-Elmer 1760X instrument under nitrogen purging.

RESULTS AND DISCUSSION

Effects of annealing temperature and time on T_m and T_g of PHB

PHB undergoes thermal degradation above its melting temperature of 172°C. This results in a drastic reduction of its molecular weight above about 190°C[29,30]. The degradation in the temperature range 180–200°C is due to the random chain scission of the six-membered ring ester:



(I)

The products of thermal degradation contain carboxyl and vinyl terminated PHB compounds[29], which can lead to acidolysis and cross-linking. Therefore, it is important to determine how the annealing temperature and duration affect the T_g and T_m of PHB, since the latter quantities provide information about the extent of degradation. The results are summarized in *Table 1*. The T_m of PHB decreases with increasing annealing temperature and duration. The T_m depression after 30 and 60 min of annealing at 190°C was 3 and 7°C respectively. This indicates that some degradation has taken place. However, the depression of T_m for annealing times less than 60 min at 180°C was very small and the samples exhibited an almost constant T_g. This indicates that the degradation was negligible. To ensure that little degradation occurs, the ultimate temperature for all DSC scannings was chosen as 180°C.

Table 1 Effects of annealing temperature and time on T_m (°C) and T_g (°C) of PHB

Annealing temperature (°C)	Annealing time (min)			
	0	1	30	60
	T_m (T_g)	T_m (T_g)	T_m (T_g)	T_m (T_g)
180	172 (3)	172 (3)	171.5 (3)	170.5 (3)
190	172 (3)	172 (3)	169 (3)	165 (3)

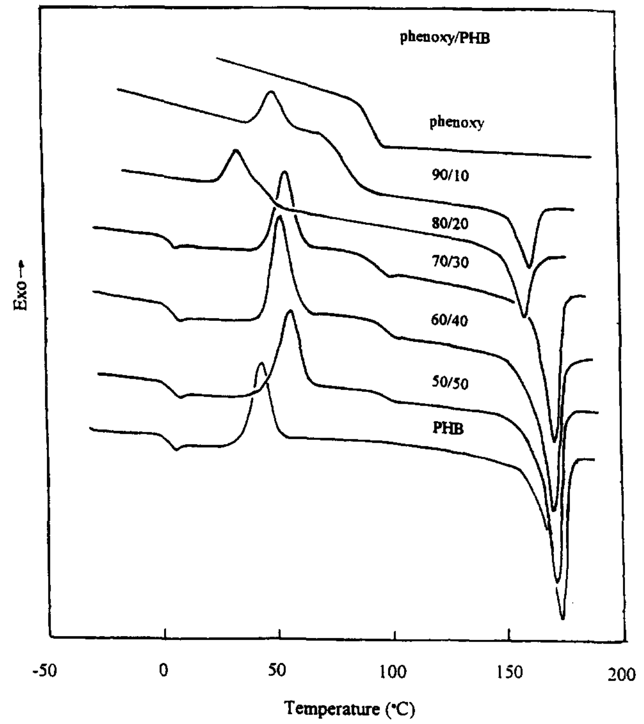


Figure 1 DSC thermograms of phenoxy, PHB and their blends, for the first kind of experiment

Miscibility of phenoxy and PHB blends

Figure 1 presents the DSC thermograms of phenoxy, PHB and their blends for the first kind of experiments (1 min annealing at 180°C followed by quenching and rescanning). Phenoxy is an amorphous polymer which exhibits a T_g at 93°C. PHB has its T_g and T_m at 3 and 172°C respectively. For the phenoxy/PHB blends, a depression of the T_m with respect to that of PHB was detected in those blends containing 10 and 20 wt.% PHB, for which the T_m values were 162 and 160°C respectively. In addition, a single T_g at about 83°C was noted for a PHB content of 10 wt.%, and no T_g could be detected for the 20 wt.% PHB sample. The depression of T_m compared to that of PHB and the existence of a single intermediate T_g indicate the formation of miscible blends at 180°C (since the quenched sample reflects the phase behavior at 180°C) as a result of the interactions between phenoxy and PHB. Either the hydrogen bonding between the secondary hydroxyl groups of phenoxy and the carbonyl groups of PHB and/or the transesterification may be responsible for the miscibility. It will be shown later that the transesterification plays an important role. For comparison, the DSC thermograms for blends containing 30%–100 wt% PHB are also included in *Figure 1*. They have two T_g values, namely those of the pure PHB and almost pure phenoxy, and the T_m (171°C) is close to that of the pure PHB. This clearly indicates that, under the conditions in which the latter experiments have been performed, the phenoxy and PHB remain largely immiscible at 180°C. In the DSC curves, an exothermal peak was detected for the melt-quenched samples, which represents the PHB exothermal cold crystallization temperature.

Figure 2 provides information about the effect of annealing at 180°C on the compatibility of the phenoxy/PHB mixture containing 10 wt.% PHB on the basis of the second kind of experiments. Curve a, obtained during the first scanning shows that two phases co-exist at room temperature in the as-prepared blend before annealing: a single amorphous phase containing phenoxy and PHB and a crystalline phase based on PHB. The sample possesses a T_g at 83°C which is lower than that of pure phenoxy and a T_m at 162°C which is lower than that of pure PHB. When the same sample was annealed at 180°C, for 10 min, quenched and scanned again, the DSC thermogram (curve b) indicated that the T_g and the T_m remained almost those of curve a. Curves c and d represent scanning traces after successive annealings of the same specimen for 20 and 30 min respectively, followed by quenchings. The T_g decreases to 68°C and the melting peak is no longer present after annealing for a total of 60 (10 + 20 + 30) min. The existence of a single T_g and the absence of a melting peak suggest the formation, after a total of 60 min of annealing at 180°C, of a single amorphous phase. This was also confirmed by the appearance of the film, which was opaque before any annealing, owing to the presence of PHB spherulites larger than the wavelength of light, and became transparent after a total of 60 min of annealing. As expected, the formation of a single phase was accelerated by a higher annealing temperature. When the same kind of sample was annealed at 190°C, the single phase was formed within 30 min of total annealing. For a mixture containing 20 wt.% PHB, about 100 min were needed to reach a single phase at 180°C. For mixtures containing larger amounts of PHB, the time needed to reach a single phase was much longer. As an example, we consider the mixture containing 30 wt.% PHB. *Figure 3* provides the DSC thermograms of a sample of the above mixture annealed successively at 180°C up to a total of 4 h. Curve a represents the second scanning, after annealing 1 min and quenching. It exhibits two T_g and one T_m. One of the T_g is for the phenoxy-rich phase, the other is for PHB. Curves b–f represent scanning traces of the same specimen after successive annealings followed by quenchings. The T_g of phenoxy and T_m decrease with increasing annealing time, indicating a trend to miscibility. The sample forms, finally, after a total of 4 h of annealing, a single phase, which exhibits a single intermediate T_g at 47°C and no melting peak, because the crystalline phase based on PHB is no longer present.

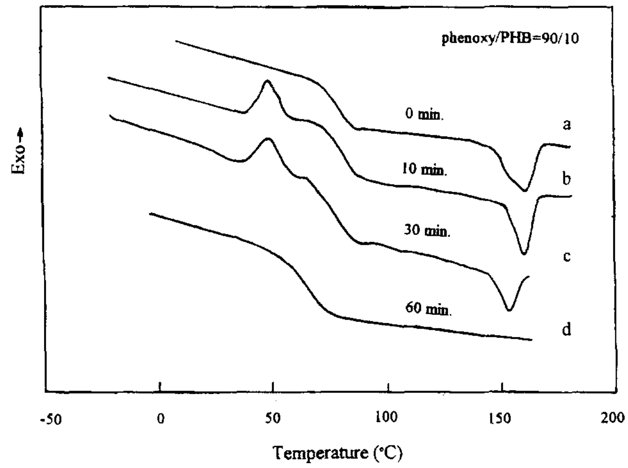


Figure 2 DSC thermograms of a phenoxy/PHB blend with 10 wt.% PHB, annealed for different times at 180°C (second kind of experiment). The times marked in the figure represent total annealing times

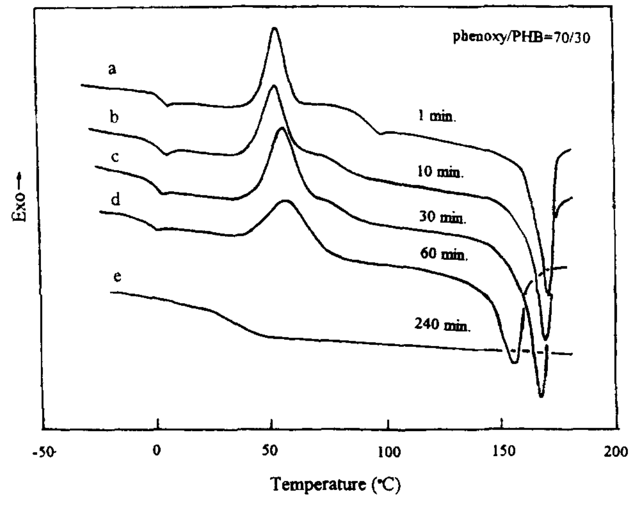


Figure 3 DSC thermograms of a phenoxy/PHB blend with 30 wt.% PHB, annealed for different times at 180°C (second kind of experiment). The times marked in the figure represent total annealing times

Effect of thermal degradation on the phenoxy/PHB blends

When the annealing takes place for a long time and at high temperatures, the PHB molecules are degraded. The thermal degradation products of PHB contain carboxyl- and vinyl-terminated PHB macromolecules. The latter can generate cross-linking. Since the homogeneous product of phenoxy/PHB of 90/10 (wt/wt) composition, annealed at 180°C for 60 min was completely soluble in THF (PHB is insoluble in THF), it is clear that in that case the cross-linking was negligible. However, for the phenoxy/PHB blends of 80/20 or 70/30 (wt/wt) composition annealed at 180°C for 100 min and 4 h respectively, insoluble fractions in THF were obtained. Since the crystalline phase of PHB which is insoluble in THF is no longer present under these conditions, only the cross-linking can be responsible for the insoluble fractions. The THF insoluble fraction is most likely due to the phenoxy/PHB cross-linking and self-crosslinking of PHB by the degradants.

*FT*i.r. spectra

Figure 4 presents the *FT*i.r. spectra in the 1550–1800 cm^{-1} range of the pure phenoxy and of the soluble fraction of phenoxy/PHB blends of 70/30 (wt/wt) composition, which were either free of annealing or were annealed at 180°C for 10, 30 and 240 min respectively, and cooled to room temperature before extraction. For the pure phenoxy, the absorptions at 1608 and 1582 cm^{-1} can be assigned to

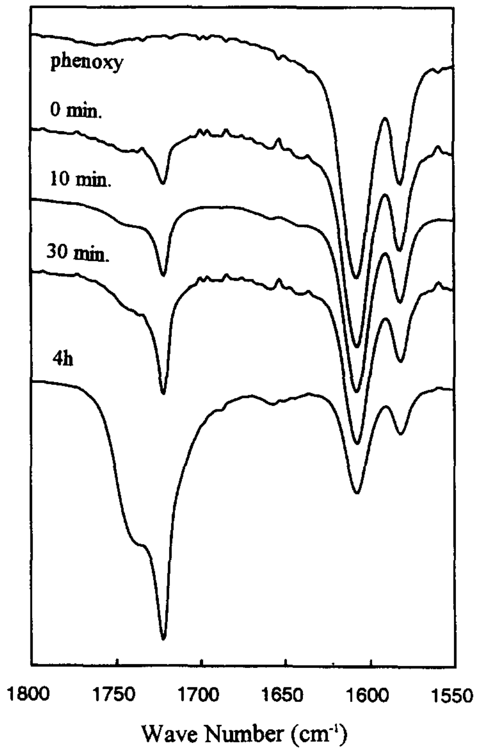


Figure 4 FTIR spectra of carbonyl stretching for phenoxy and THF soluble fractions of blends with 30 wt.% PHB annealed for various times (marked in the figure) at 180°C

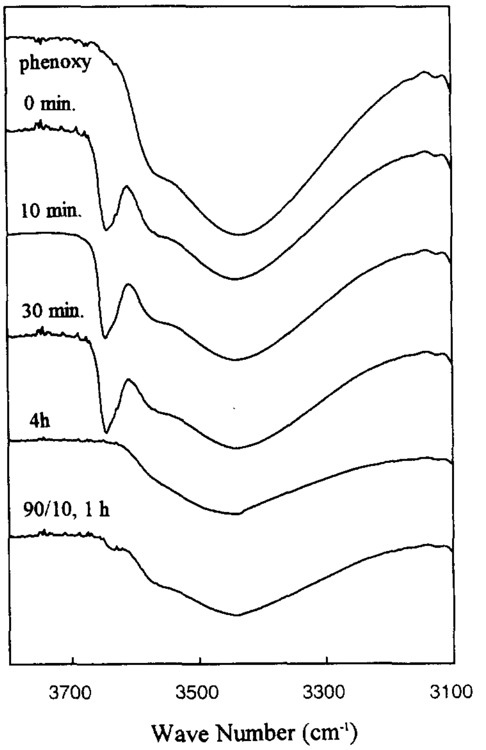


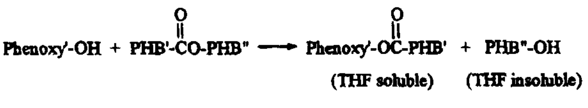
Figure 5 FTIR spectra of hydroxyl stretching for phenoxy and THF soluble fractions of blends (phenoxy/PHB 70/30 (wt/wt)) annealed for various times (marked in the figure) at 180°C

the para-substituted benzene ring moiety; as expected, no carbonyl absorptions are present. For the blend free of annealing, a small peak at 1722 cm^{-1}, which is characteristic of the carbonyl stretching, is present in the THF soluble fraction, indicating the presence of PHB. There are two possibilities: (a) traces of THF soluble PHB are physically mixed with phenoxy; (b) transesterification has occurred during the preparation of the sample and the two polymers are chemically linked. The latter possibility is selected, for reasons which will be discussed later.

The ratio of the intensities of C=O and of benzene ring absorptions (I_{co}/I_{ben}) increases with increasing annealing time, demonstrating that the PHB content in the THF soluble fraction increases with increasing annealing time. This indicates that the PHB, which is insoluble in THF, reacts via transesterification with phenoxy, which is soluble in THF, generating a graft copolymer which is soluble in THF. (It is possible for the soluble fraction to contain also low molecular weight PHB chains formed during transesterification.) The thin films cast on NaCl plates from the THF soluble fractions are opaque for the samples annealed between 0 and 30 min, indicating that they are heterogeneous. In contrast, for those annealed for sufficiently long times, the films cast from the soluble fractions are transparent, indicating that PHB moieties are randomly grafted to the phenoxy chains as a result of transesterification. These results suggest that for short annealing times, the soluble fraction has a structure which is different from that at long annealing times. In other words the grafting of PHB to phenoxy leads to different structures at short and long annealing times.

Figure 5 presents the *FT*i.r. spectra in the hydroxyl stretching range of the phenoxy and of the THF soluble fractions of the blends after annealing for various lengths of times. Three peaks are possible: a broad one at 3435 cm^{-1}, which can be assigned to the multi-hydrogen-bonded OH stretching, a shoulder at 3550 cm^{-1}, which can be attributed to the hydrogen-bonded dimer stretching, and a sharp peak at 3630 cm^{-1}, which can be assigned to the free non-hydrogen-bonded OH groups[7]. Only a broad peak at 3435 cm^{-1} and a shoulder at 3550 cm^{-1} are present for the pure phenoxy. This indicates that all the OH groups in phenoxy are involved in self-association. It is important to note that all three peaks are present in the THF soluble fractions of the blends (70/30 wt/wt) annealed for 0, 10 and 30 min, which as noted above are heterogeneous. In contrast, in the homogeneous blends (70/30, 4 h annealing and 90/10, 1 h annealing), all the OH groups are hydrogen bonded as in the pure phenoxy. The difference in hydroxyl stretching between the heterogeneous and homogeneous samples is obvious. This can be explained as follows.

In the present case, the reaction occurs at 180°C and the thermal degradation is negligible for annealing times shorter than 60 min. Under such conditions, the intermolecular alcoholysis II, which yields a graft copolymer, is expected to be dominant.



$$\text{Phenoxy'-OH} + \text{PHB'-}\overset{\overset{\displaystyle O}{\|}}{C}\text{O-PHB''} \longrightarrow \underset{\text{(THF soluble)}}{\text{Phenoxy'-O}\overset{\overset{\displaystyle O}{\|}}{C}\text{-PHB'}} + \underset{\text{(THF insoluble)}}{\text{PHB''-OH}} \qquad \text{(II)}$$

Since the graft copolymer promotes the miscibility of the two incompatible polymers, the T_g of the phenoxy-rich phase and the T_m of the PHB based phase should decrease with increasing annealing time, and the T_m should no longer be present when the blends reach homogeneity. This is, indeed, observed experimentally (see *Figures 2 and 3*).

The THF soluble fraction contains the unreacted phenoxy and the graft copolymer. Since a fraction of the OH groups of the phenoxy are randomly substituted by PHB segments, the intermolecular and intramolecular interactions among the remaining OH groups of phenoxy are impeded, and consequently, less hydrogen bonding among them will take place. Indeed, *Figure 5* shows that for short annealing times (0–30 min) there are free OH groups and that the PHB moieties grafted to the phenoxy chain impede the hydrogen-bonding. However, for the homogeneous samples (phenoxy/PHB 90/10 and 70/30 after annealing for a total of 1 and 4 h respectively), the soluble fractions contain a large amount of PHB moieties (as revealed by the high ratio of I_{co}/I_{ben} in the *FT*i.r. spectra, see *Figure 4*) and all the hydroxyl groups present are hydrogen bonded (see *Figure 5*). These observations suggest that the structure of the PHB moieties grafted to the phenoxy chains is different in the specimens annealed for short and long times. Those annealed for a long time contain a large number of melted, more flexible, grafted PHB moieties and the remaining OH groups of the phenoxy can form hydrogen bonding with the C=O groups of these flexible moieties. In contrast, for short annealing times, the PHB moieties maintain their crystalline structure and being more rigid are less susceptible for hydrogen-bonding.

As mentioned before, both carbonyl and free hydroxyl groups were detected in *FT*i.r. of the sample free of annealing. This happens because some transesterification has taken place during the stages of dissolution and casting of the preparation of the sample (the physically mixed PHB and phenoxy cannot have non-hydrogen-bonded OH groups, because neither of them has such groups).

CONCLUSION

The miscibility and transesterification of poly(hydroxyl ether of bisphenol A) (phenoxy) and biodegradable poly(3-hydroxybutyrate) (PHB) blends prepared by solution casting were investigated by means of DSC and *FT*i.r. During heating from room temperature to 180°C at a rate of 10°C $\min^{-1}$, the phenoxy/PHB blends were miscible for PHB contents less than 20 wt.% and immiscible for higher contents. Transesterification can generate single-phase blends when it is sufficiently advanced. The *FT*i.r. investigations have demonstrated that all OH groups of pure phenoxy are involved in hydrogen-bonding and that with increasing annealing time at 180°C of the phenoxy/PHB blends, the number of non-hydrogen-bonded OH groups first increases, passes through a maximum and becomes negligible once a single-phase blend is formed. This happens for the following reasons. For short annealing time, the PHB moieties grafted to the phenoxy chains keep their crystalline structure and, as a result, they impede both the hydrogen-bonding among the OH groups of phenoxy and between the OH groups of phenoxy and C=O groups of PHB. For long annealing times, the grafted PHB moieties are 'melted', hence flexible, and the hydrogen bonding between the OH of phenoxy and C=O of PHB becomes possible.

REFERENCES

1. Olabishi, O., Robeson, L. M., Shaw, M. T., Polymer–Polymer Miscibility, Academic Press, New York, 1979.
2. Utracki, L. A., Polymer Alloys and Blends, Hanser, Munich, 1989.
3. Nishi, T., Wang, T. T. and Kwei, T. K., *Macromolecules*, 1975, **8**, 227.
4. Tan, L. S., Arnold, F. E. and Chaun, H. H., *Polymer*, 1991, **32**, 1376.
5. Lu, X. and Weiss, R. A., *Macromolecules*, 1991, **24**, 4381.
6. Eisenberg, A., Smith, P. and Zhou, Z. L., *Polym. Eng. Sci.*, 1982, **22**, 1117.
7. Coleman, M. M. and Painter, P. C., *Prog. Polym. Sci.*, 1995, **20**, 1.
8. Porter, R. S. and Wang, L. H., *Polymer*, 1992, **33**, 2019.
9. Murff, S. R., Barlow, J. W. and Paul, D. R., *J. Appl. Polym. Sci.*, 1984, **29**, 3231.
10. Wahrmund, D. C., Paul, D. R. and Barlow, J. W., *J. Appl. Polym. Sci.*, 1978, **22**, 2155.
11. Choi, G. D., Kim, S. H., Jo, W. H. and Rhim, M. S., *J. Appl. Polym. Sci.*, 1995, **55**, 561.
12. Robeson, L. M. and Furtek, A. B., *J. Appl. Polym. Sci.*, 1979, **23**, 645.
13. Dawes, E. A., Microbial Energetics, Blackie, Glasgow, 1986.
14. Doi, Y., Microbial Polyesters, VCH, New York, 1990.
15. Sharma, R. and Ray, A. R., *Rev. Macromol. Chem. Phys.*, 1995, **C35**(2), 327.
16. Barham, P. J., Keller, A., Otun, E. L. and Holmes, P. A., *J. Mater. Sci.*, 1984, **19**, 2781.
17. Avella, M. and Martuscelli, E., *Polymer*, 1988, **29**(10), 1731.
18. Greco, P. and Martuscelli, E., *Polymer*, 1989, **30**, 1475.
19. Marand, H. and Collins, M., *Polym. Prep. Am. Chem. Soc.*, 1990, **31**, 552.
20. Paglia, E. D., Beltrame, P. L., Canetti, M., Seves, A., Maracandalli, B. and Martuscelli, E., *Polymer*, 1993, **34**(5), 996.
21. Kumagai, Y. and Doi, Y., *Polym. Degrad. Stab.*, 1992, **36**, 241.
22. Koyama, N. and Doi, Y., *Can. J. Microbiol.*, 1995, **41**(suppl. 1).
23. Lotti, N., Pizzoli, M., Ceccorulli, G. and Scandola, M., *Polymer*, 1993, **34**(23), 4935.
24. Seves, A., De Marco, T., Cimmino, S., Martuscelli, E. and Silvestre, C., *Macromolecules*, 1995, **28**, 8065.
25. Bain, P. R., Goodwin, A. A. and Hay, J. N., *Macromol. Rep.*, 1994, **A31**, 1135.
26. Bloembergen, S., Holden, D. A., Hamer, G. K., Bluhm, T. L. and Marchessault, T. L., *Macromolecules*, 1986, **19**, 2865.
27. Reeve, M. S., McCarthy, S. P. and Gross, R. A., *Macromolecules*, 1988, **21**, 2657.
28. Robeson, L. M., *J. Appl. Polym. Sci.*, 1985, **30**, 4081.
29. Grassie, N., Murray, E. J. and Holmes, P. A., *Polym. Degrad. Stab.*, 1984, **6**, 47.
30. Kunioka, M. and Doi, Y., *Macromolecules*, 1990, **23**, 1933.