Thermal Oxidation of Self-Degradable Composite Films Based on Low-Density Polyethylene

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ABSTRACT: The effect of the structure of composite extrusion films based on a mechanical blend of low-density polyethylene and poly(hydroxybutyrate) on the service characteristics and the kinetics of thermooxidative destruction was investigated. The aggregate state of the polymers affected the value of the boundary surface in the blend films. An increase in the latter affected the conformation states of both polymers in the blends. In this case, the strength decreased, the steam permeability increased, and the thermooxidative destruction of the polyethylene matrix during the beginning stages was accelerated. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1392–1396, 2004

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INTRODUCTION

At this time, composite materials based on traditional synthetic polymers and new biodegradable polymers are attracting much interest. For destructible components, different biopolymers can be used, such as polylactones[1] and polyorthoesters.[2] Among the latter, polyalkanoates[3] and their typical representative, poly(hydroxybutyrate) (POB), should be mentioned. Composites of such a type are, as a rule, thermodynamically incompatible blends. These blends are characterized by a polydisperse structure with a developed boundary surface (BS) between phases. The polydispersity of the compositions and, therefore, the length of the interphase boundary in the blends depend on the nature of the contacting polymers,[4] their rheology,[5] the cohesion forces that characterize the intermolecular interaction,[6] and the mixing technology (rate, stress, and temperature).[7] During the formation of the blends, the component structure undergoes significant changes on the molecular, supramolecular, crystalline, and macro levels in comparison with the original polymers. The component structure determines both the value and geometry of the BS and the depth of the boundary layer. The BS parameters affect the service properties and kinetics of the diffusion and chemical processes, particularly the processes of composite oxidation.[4]

Considering the important role of chemical stability in the reaction of air and oxygen, we aimed in this work to establish a relationship between the morphology of heterogeneous blend films based on a blend of low-density polyethylene (LDPE) and POB and their kinetics of oxidation.

EXPERIMENTAL

LDPE (PENP, 15803-020, Russia), with a molecular weight of 2.5×10^5, was used in the form of 2–3-mm granules and in the form of a powder with a particle size of 5–10 mkm. POB (Biomer, Germany), with a number-average molecular weight of $2.0-10^5$, was used as a powder with a particle size of 7–12 mkm. A polyethylene (PE)/POB (92/8 mass % ratio) composition was prepared in the following way. With a ball mill, granulated PE was mixed mechanically with POB powder, and powdered PE was mixed with powdered POB. With a one-screw laboratory granulator (length/diameter = 20, diameter = 20 mm, velocity = 100 rpm, temperature = 125°C), blended granules were obtained. Then, the granules were put into an aggregate to make an АРП-20 hose-type film (diameter = 20 mm, length/diameter = 25, velocity = 100 rpm, temperature along the extruder zones < 185°C), and the film hose was formed. The thickness of the film along the perimeter was 45 ± 5 mkm at a drawing ratio of 5, and the state of expansion by air was 2.

The POB state of dispersity in the samples was determined by raster electron microscopy on the longitudinal across crushed sample surfaces (toward the extrusion direction) at a magnitude of 100–10,000. The

electron microscope was a BS-301 (Tesla, United States). The heat and physical parameters of the blends were determined with a DCM-2 differential scanning calorimeter at a scanning rate of 16°/min. The calibration of the temperature scale was based on the indium melting temperature of 156.5°C; the sample weight was 14–15 mg. The structure and state of orientation of the polymer chains were determined with Fourier transform infrared spectroscopy; the device was a Bruker (Germany) IFS-48 instrument. For this purpose, we used the following structure-sensitive absorbency bands: 729 cm^{-1} (the band connected to PE crystallinity[8]) and 1228 cm^{-1} (the band connected to POB crystallinity[9]). The spectra were registered in polarized light. The beam was polarized along and perpendicular to the extrusion direction. The optical density (D_o) of each band was determined with the following formula:

$$D_0 = D_{\text{II}} + 2D_{\perp}/3$$

where $D_{\parallel}$ is the optical density along the extrusion direction and $D_{\perp}$ is the optical density perpendicular to the extrusion direction. The molecular orientation was evaluated according to the dichroic ratio ($R = D_{\parallel}/D_{\perp}$) of the structure-sensitive bands.

The strength properties of the films were determined according to GOST, 14236-81 (Russia). The water penetration at 18°C was determined according to a reported procedure.[10] The oxygen absorption was measured with a manometric device.[11]

RESULTS AND DISCUSSION

Microscopy investigations of the PE/POB blends showed that the POB phase had clearly defined boundaries. This provided evidence of the absence of a noticeable transition interphase layer. Figure 1 shows the size distribution curves of the POB phase in PE. On the basis of obtained microphotographs and the Kavaliery–Akker[7] principle, the average sizes of the POB phase were calculated. After that, differential distribution curves were built. The data showed that the average size of POB in the films formed from the granule–powder system was about 1.0 mkm. In the films prepared from the powder–powder system, the average size was 0.3–0.6 mkm. Because the concentration of POB in the compositions was the same, the films prepared through the blending of the two powders had a more developed specific BS. Because we did not observe a developed interphase layer, we believe that all the effects that we describe in this article were related to the value of BS between the two phases. In our case, the determining value included the particle size of the dispersion phase and the length of the boundary between phases. This has been confirmed by literature data,[5,12] which demonstrate the
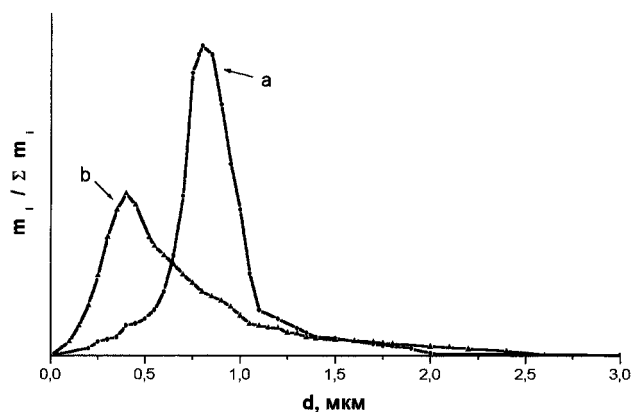
Figure 1 Dependence of the size distribution curves of POB particles [diameter (d)] in blend films on the initial aggregate state of blended LDPE and POB particles: (a) LDPE granules and POB powder and (b) LDPE powder and POB powder.

relationship between the initial particle size of a dispersion phase and the final dispersity of a composite, which affects the service property level. A more dispersed structure forms during the blending of same-particle-size components. If the system components have quite different particle sizes, their behavior during blending will be different under the action of gravitational forces on particles with significantly different masses.

From the published data, we know that BS can significantly affect the strength properties[7] and compound transport characteristics[13] of polymeric materials. To evaluate the role of BS on the structure and properties of films based on LDPE/POB, we determined the structural parameters (the crystallinity and orientation state of the crystalline-phase macromolecules) and service properties (the strength and water penetration) of the films (see Table I).

The data in Table I show that the composite films had reduced tensile strength values and increased values of water penetration in comparison with pure PE films. The lowest strength and highest water penetration were found in the films with the largest BS values. This was explained by the absence of an interphase layer. In this case, the structure of the polymers in the proximity of the boundary was less dense than that in the volume. Moreover, the components by themselves could form microscopic channels along the phase boundary, and this could occur over the course of film drawing and the expansion of the film hose. It is known from the literature that supramolecular structures and molecular orientation in polymer blends and the character of component interactions[11,14] significantly affect oxidative processes. For this reason, we conducted investigations of the crystalline and molecular structures of the LDPE/POB blends.

TABLE I
Structural and Service Parameters of Films Based on LDPE and POB

System type	Melting temperature (°C)	Crystalinity state %	Tensile strength (MPa)[a]	Water permeability at 18°C (10^8 cm/ cm hr mmHg)	Optical density (rel. units)		Dichroism (rel. units)	
					Band at 729 cm^{-1}	Band at 1228 cm^{-1}	Band at 729 cm^{-1}	Band at 1228 cm^{-1}
LDPE granules and POB powder	105.0[b]	21.8	18.0	5.52	1.460	1.420	0.939	1.400
POB powder	171.2[c]	31.4						
LDPE powder and POB powder	106.0[d]	19.1	15.6	11.6	1.420	1.520	1.070	0.720
POB powder	172.0	31.4						
LDPE	107.0	35.0	20.0	2.38	1.500	—	1.750	—
POB	175.4	70.0	40.0	0.013	—	5.860	—	2.500

[a] Along the extrusion direction.
[b] For LDPE granules only.
[c] For POB powder only.
[d] For LDPE powder only.

The data in Table I show that the melting temperatures of the components did not depend on the BS value (the state of dispersity) and did not differ from the characteristic values of films obtained from the original homopolymers. This confirms once more that in the blend films there was no intermolecular interaction between LDPE and POB that would lead to the formation of a clearly expressed interphase layer.

The state of crystallinity of the blend components decreased in comparison with the values of the original homopolymers. This decrease was probably related to the intermolecular interaction of components at the interphase boundary, that is, to the effect of BS on structure formation.

A change in chain conformation (Table I) also affects structure formation. For this reason, we used the data from polarized infrared spectroscopy to investigate the molecular orientation of the components in the blends. The D_o values of the crystalline blends were well correlated with the DSC data and confirmed the amorphization of the polymer crystalline phases in the blends in comparison with the homopolymers (Table I). The existence of molecular formation orientation, determined by the dichroism of the absorbency bands, indicated the blend component interactions at the interphase boundary, and it could be used for qualitative evaluations. Table I also shows that the state of PE orientation in the polymer blend films decreased in comparison with that of films of the original PE, but it did not depend on the BS value. The change in the orientation of the crystalline region in the PE matrix was probably due to the change in the relaxation rate caused by intermolecular interactions at the forming boundary layer (adhesion layer) in the blends with

POB. The data in Table I also show that the state and direction of the orientation of the POB crystalline regions of the phase in PE significantly depended on BS, and they also differed from the parameters of the original POB film. It can be concluded that the change in the spatial orientation of the macromolecules in the POB crystallites and the crystallizing process rate was mainly a function of the state of the composite dispersity. In other words, the smaller the average particle size was of the disperse phase, the greater the effect the BS value had, and it was connected to the value of the adhesion layer of the disperse phase structure. This regularity supports the following statement: the average particle size of the POB phase decrease in two times corresponded to the difference in the orientation states of the POB crystalline phase also in two times. Through a comparison of the orientation states of PE and POB in the blend films with different areas of BS, we could note the discrepancy in the numeric values of the orientation parameters (R) of these phases, which was probably connected to the different rates of the relaxation processes occurring in the PE matrix and in the POB phase during film formation. This indirectly shows the absence of the transition layer (interphase layer) in the blends, that is, the absence of intermolecular interactions of the PE phase with the POB phase in the compositions.

The macromolecules located directly in the vicinity of the phase boundary had less mobility than the molecules in the polymer volume. The effect of BS was transformed into the polymer phase volume caused by intermolecular interactions.[5] The effect of BS was also revealed in the retardation of the relaxation and crystallization processes.[14] As mentioned previously,
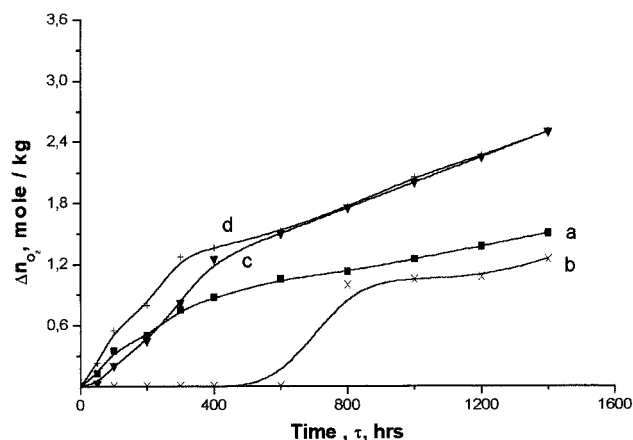
Figure 2 Kinetic curves of the oxygen absorption (Δn_{O_2}) with the oxidation time (τ) for film samples of (a) LDPE, (b) POB, (c) a blend of PE granules and POB powder, and (d) a blend of PE powder and POB powder.

we could not find a transition layer in the investigated blends. For this reason, we could assume the existence of only a thin adsorption layer less than 5–10 nm thick.[15] This layer did not show the properties of a separate phase because of its small thickness in comparison with the thickness of the boundary layer adjacent to the phase boundary.

According to the theory of adhesion interaction,[5] on the BS, the macromolecules are in the oriented state. The cohesion strength increases, and this causes a change in the chain conformation and, therefore, a reduction in the freedom state of the macromolecule segment. As shown in Table I, the PE crystallinity state in the blends practically did not change with the BS value. The PE matrix possibly had a low sensitivity toward the change in crystallinity in the BS because of the small content of POB. On the contrary, the state of POB phase crystallinity changed as the BS value changed. In the blends with a higher value of BS, the POB phase had higher crystallinity. This effect could be explained by the different course of the structure formation processes on the molecular level during the polymer melt flow and the film sample formation.

On this basis, we assumed that the state of dispersion of the biodegradable polymer POB in the LDPE matrix would affect the kinetics of the oxidation process of the composite film materials based on their blends; we observed this from the data shown in Figure 2.

The data in Figure 2 show the kinetic curves of oxygen absorption for samples of PE, POB, and their blends. The kinetics of oxidation for the blend samples differed significantly from the kinetics of oxidation for the homopolymer samples, and the kinetics deviated from each other. At deep states of oxidation (>0.5 mol/g), a sample with a higher BS value was practically oxidized with the same rate as a sample with a lower BS value, but both were oxidized significantly more quickly than the original PE.

During the beginning of oxidation (<0.5 mol/g), samples with a higher BS value were oxidized more quickly than the original PE sample, and the sample with a lower BS value and the original POB sample did not oxidize at all in the range of temperatures studied. This was confirmed by the value of the oxidation induction period. The last one was accepted to be the time until the branching of the oxidation process (when the process became autoaccelerated) and the change in the oxygen absorption rate in time.

Through a comparison of the induction period and the rate of oxygen absorption with the value of BS, we found that the sample with the more developed BS had the highest oxidation rate. First, this was connected to the fact that POB at elevated temperatures (processing and thermal oxidation) underwent destruction and, therefore, was the potential source of the low molecular radicals, which could initiate the oxidation in the PE matrix[16] caused by phase contact on the boundary and the free valence transformation. This initiated the oxidation process in the composite volume.

Second, the higher the specific BS value was, the larger the contact area was of the POB phase with the PE matrix and the higher the stress was of macromolecules in the polymer layers adjacent to the BS. As shown by the data in Table I, the orientation state of the PE phase with a large BS value was larger than that with a smaller BS value. The PE macromolecule state of orientation increase led to a decrease in the oxidation resistance.[17] This explained the high oxidation rate for a larger BS value.

As shown, the character of the PE/POB blend structure parameters changed on the molecular level in such a way that a reduction in the reaction ability of the blends was expected. It is known that a decrease in segmental mobility, that is, an enrichment of the polymer chains by straightened conformations, retards oxidative processes.[18] In our case, we observed the opposite effect. This was connected, as mentioned before, to the increase in the polymer chain stress in the proximity of the BS. At the same time, POB could suffer thermooxidative destruction (during processing) and be the source of low molecular radicals; therefore, POB could be the initiation factor. In other words, it could initiate the PE oxidation reactions. In blends of different polymers, such effects have been observed.[19] The effect depends on the BS value.

As shown in Figure 2, at low oxidation states (during the beginning of oxidation), the process kinetics were different for the blends. In the blends with a low BS value, the rate of oxidation was lower. At the same time, the original POB did not oxidize. Dissimilar behaviors of the blends during oxidation were found in the sequence of the conformational changes in the

PE matrix on the molecular level under the action of the POB phase. Apparently, during deep oxidation stages (oxidation time > 700 h), POB began to oxidize, forming low molecular radicals, which accelerated the polymeric matrix oxidation process. This was supported by a jump in the POB oxidation curve. In this case, the kinetic curves of the blends came close to one another and became more linear. This demonstrated the independence of the oxidation process of the blends from the state of dispersity (BS) because the number of radicals formed by the POB phase was the same in both blends because the content of POB in the compositions was the same.

CONCLUSIONS

On the basis of the obtained results, we concluded the following:

- The aggregate state of the original polymers affected the value of BS. The BS increase in the films based on the LDPE/POB blend reduced the physical properties and significantly increased the transport characteristics.
- The state of the POB crystalline phase depended on the value of BS: the greater BS was, the higher the crystallinity state was.
- The state of dispersity of POB was assumed to affect the processes of the molecular orientation of the crystalline phase.

Thus, the BS increase changed the conformational state of the polymers in the blends on different levels of structural organization. This accelerated the effects on the thermal destruction during the beginning stage.

This regularity was also expected with secondary LDPE.

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