Introdaction Composite materials based on biodegradable polymers are currently evoking great scientific and practical interest. Among these polymers is poly(3-hydroxybutyrate) (PHB), which belongs to the class of poly(3-hydroxyalkanoates). Because of its good mechanical properties (close to those of PP) and biodegradability, PHB has been intensely studied in the literature [1]. However, because of its significant brittleness and high cost, PHB is virtually always employed in the form of blends with starch, cellulose, PE [2], etc., rather than in pure form. This work is concerned with the study of the structural features of PHB-EPC blends and their thermal degradation. Experimental The materials used in this study were EPC of CO-059 grade (Dutral, Italy) containing 67.4 mol % ethylene units and 32.6 mol % propylene units. PHB with Мц = 2.5 x 105 (Biomer, Germany) was used in the form of a fine powder. The PHB : EPC ratios were as follows: 100 : 0, 80 : 20, 70 : 30, 50 : 50, 30 : 70, 20 : 80, and 0: 100 wt%. The preliminary mixing of the components was performed using laboratory bending microrolls (brand VK-6) under heating: the microroll diameter was 80 mm, the friction coefficient was 1.4, the low-speed roller revolved at 8 rpm, and the gap between the rolls was 0.05 mm. The blending took place at 150°C for 5 min. Films were prepared by pressing using a manual heated press at 190°C and at a pressure of 5 MPa; the cooling rate was ~50°C/min. The thermophysical characteristics of the tested films and the data on their thermal degradation were obtained using a DSM-2M differential scanning calorimeter (the scanning rate was 16 K/min); the sample weight varied from 8 to 15 mg; and the device was calibrated using indium with Tm = 156.6°C. To determine the degree of crystallinity, the melting heat of the crystalline PHB (90 J/g) was used [2]. The Tm and Ta values were determined with an accuracy up to 1°C. The degree of crystallinity was calculated with an error up to ±10%. The structure of polymer chains was determined using IR spectroscopy (Specord M-80). The bands used for the analysis were structure-sensitive bands at 720 and 620 cm-1, which belong to EPC and PHB, respectively [3]. The error in the determination of reduced band intensities did not exceed 15%. Results and discussion The melting endotherms of PHB, EPC, and their blends are shown in Fig. 1. Apparently, all the first melting thermograms (except for that of EPC) show a single peak characteristic of PHB. The thermophysical characteristics obtained using DSC for blends of various compositions are listed in Table 1. As is apparent from this table, the melting heat rHml of PHB during first melting changes just slightly in comparison with the starting polymer. During cooling, only a single peak corresponding to the crystallizing PHB additionally appears. However, the repeated melting endotherms of some blends (70% PHB + 30% EPC, 50% PHB + 50% EPC) display a low-temperature shoulder. Note that the melting enthalpy significantly changes as one passes from an EPC-enriched blend to a composition where PHB is predominant. When the content of EPC is high, the melting heat AHm2 of the recrystallized PHB significantly decreases. This effect should not be regarded as a consequence of the temperature factor, because the material was heated up to 195°C during the DSM-2M experiment and the films were prepared at 190°C; the scanning rate was significantly lower than the cooling rate during the formation of the films (50 K/min). Thus, the state of the system after remelting during DSC measurements is close to equilibrium. These results make it possible to assume that the melting heat and the degree of crystallinity of PHB decrease in EPC-enriched blends due to the mutual segmental solubility of the polymers [4] and due to the appearance of an extended interfacial layer. Also note that the degree of crystallinity may decrease because of the slow structural relaxation of the rigid-chain PHB. This, in turn, should affect the nature of interaction between the blend components. However, the absence of significant changes in the Tm and Ta values of PHB in blends indicates that EPC does not participate in nucleation during PHB crystallization and the decrease in the melting enthalpy of PHB is not associated with a decrease in the structural relaxation rate in its phase. Thus, the crystallinity of PHB decreases because of its significant amorphization related to the segmental solubility of blend components and to the presence of the extended interfacial layer. Fig. 1 - The melting endotherms of (1) PHB, (2) EPC, and their blends with compositions (3) 80 : 20, (4) 70 : 30, (5) 50: 50, (6) 30: 70, and (7) 20: 80 wt % Table 1 - The thermophysical properties of PHB-EPC films PHB:EPC, wt % Tm, ºC Tcr, ºC Degree of crystallinity**, % J/g 100:0 174 88.3 88.9 64 98 80:20 173 75.8 76.2 64 84 70:30 172 59.5 60.1 60 66 50:50 172 56.4 52.1 62 63 30:70 172 29.3 20.5 60 33 20:80 171 22.3 15.7 - 25 0:100 - - - - - * Calculated as areas under the melting curves: the first melting and the melting after the recrystalization, respectively, ** Calculated according to the values. Figure 2 shows the IR spectra for two blends of different compositions. As is known, the informative structure-sensitive band for PHB is that at 1228 cm-1 [5]. Unfortunately, the intensity of this band cannot be clearly determined in the present case, because it cannot be separated from the EPC structural band at 1242 cm-1 [3]. The bands used for this work were the band at 620 cm-1 (PHB) and the band at 720 cm-1 (EPC) [6], which correspond to vibrations of C-C bonds in methylene sequences (CH2), where n > 5, occurring in the trans-zigzag conformation. The ratios between the optical densities of the bands at 720 and 620 cm-1 (D720/D620) are transformed in the coordinates of the equation where (5 is the fraction of EPC and W is the quantity characterizing a change in the ratio between structural elements corresponding to regular methylene sequences in EPC and PHB. Figure 3 demonstrates the value of W plotted as a function of the blend composition. Apparently, this dependence is represented by a straight line in these coordinates but shows an inflection point. The latter provides evidence that phase inversion takes place and that the nature of intermolecular interactions between the polymer and the rubber changes.

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the nature of intermolecular interactions between the polymer and the rubber changes. The phase inversion causes the blends in question to behave in different ways during their thermal degradation. The DSM-2M traces (Fig. 4) were measured in the range 100-500°C. The thermograms of the blends display exothermic peaks of the thermal oxidation of EPC in the range 370-400°C and endothermic peaks of the thermal degradation of PHB at T> 250°C. For the pure PHB and EPC, the aforementioned peaks are observed in the ranges 200-300°C and 360-430°C, respectively. Fig. 2 - The IR spectra of PHB-EPC blends with compositions (a) 80 : 20 and (b) 20 : 80 wt % The blend samples studied in this work display two peaks each, thus confirming the existence of two phases. Note that the peak width increases (curves 3, 4 in Fig. 4), and the heat Q of the thermal degradation of PHB changes in all the blends studied here (Table 2). This effect is apparently determined by the blend structure rather than by its composition. In blends, PHB becomes more active compared to the pure polymer and the rate of its thermal degradation increases. The temperature corresponding to the onset of thermal degradation 7^ decreases from 255°C; the value characteristic of the pure PHB, to 180°C (Table 2). The structure of the polymer becomes less perfect in this case; two likely reasons for this are a change in the morphology and the appearance of an extended interfacial layer. As to EPC, it acquires a higher thermal stability in the blends under examination, as indicated by the increase in the temperature corresponding to the onset of its thermal oxidation 7o (Table 2). The position of the exothermic peaks on the temperature scale characteristic of EPC indicates that its activity in blends is lower than that in the pure sample. The low-temperature shoulder of the exothermic EPC peak in the range 360-380°C (Fig. 4) decreases with increasing content of PHB. Apparently, this effect is due to a change in the copolymer structure related to the interpenetration of PHB and EPC segments. Fig. 3 - Plot of W vs. the content of PHB in the blend Fig. 4 - The DSC traces of (1) PHB, (2) EPC, and their blends with compositions (3) 70 : 30 and (4) 30 : 70 wt % Table 2 - The parameters of the thermal degradation process PHB:EPC, wt % Tod(EPC), ºC Tod(PHB), ºC Q*(PHB), kJ/g 100:0 - 255 0.53 70:30 370 180 1.38 30:70 380 250 0.51 0:100 360 - - * The specific heat of thermal dergradation per g of PHB Thus, the existence of two peaks in DSC thermograms of the blends indicates the presence of two phases in the PHB-EPC blends. The phase inversion takes place in the vicinity of the composition with equal component weights. The components influence each other during film formation, and, hence, the appearance of the extended interfacial layer is presumed for samples containing more than 50% EPC. A change in the structure of the blends affects their thermal degradation. The degradation of PHB in blends is more pronounced than that in the pure PHB, but the thermal oxidation of EPC is retarded.