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Influence of thermal degradation on tensile strength and Young's modulus of poly(hydroxybutyrate)

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SUMMARY

Microbially produced poly(3-hydroxybutyrate) (P(3HB)) and a copolymer were investigated by measuring tensile strength, Young's modulus and molar mass after different periods of thermal treatment at temperatures slightly above their melting temperatures in order to describe the changes of molecular and mechanical properties. The tensile strength turns out to be strongly influenced by time and temperature of heat treatment. After a heat treatment for 10 min at 190 °C the tensile strength drops to 30% of its initial value.

INTRODUCTION

Microbially produced polyesters, like P(3HB), belong to the family of thermoplastic polymers having a high degree of crystallinity and a well-defined melting endotherm at about 180 °C /1/. Applications of biodegradable polyesters include agricultural mulching films and packaging films as well as bottles and containers /2/. Furthermore, medical applications are well known, e.g. in cases of controlled drug release /3/, surgical sutures /4/ and bone plates /5/.

P(3HB) homopolymer is thermally unstable in the melt and degrades to crotonic acid when kept at temperatures slightly above its melting temperature of about 180 °C /6/ for a relatively long period. The melting temperatures of PHB copolymers are lower than the melting temperature of pure P(3HB) depending on comonomer content. As has been pointed out PHB copolymers are thermally stable in the melt at temperatures below 160 °C, and conventional processing methods of thermoplastics can be used /7/.

Assuming that the chain scission is completely random and no volatilization occurs during thermal degradation of the PHB samples, the number average of the degree of polymerization at time t, ($P_{n,t}$), is given by the following equation,

$$\frac{1}{P_{n,t}} - \frac{1}{P_{n,0}} = k_d t \qquad [1]$$

where $P_{n,0}$ being the number average of the degree of polymerization and k_d beeing the rate constant of thermal degradation (first order process). It is well known that molar mass is reduced by thermal degradation, but little information exists on the influence of thermal degradation on the tensile strength and Young's modulus of P(3HB).

EXPERIMENTAL

Materials

Investigations were made on native powders of P(3HB) produced by Petrochemie Danubia (Austria) with a melting temperature of 176 °C and a crystallinity of 80% as measured by X-ray and on P(3HB-co-5 mol%3HV) copolymer produced by ICI (UK) containing 5mol% of hydroxyvalerate characterized by a melting temperature of 163 °C and an X- ray crystallinity of 75%.

Thermal treatment and sample production

Films were produced in a temperature-controlled hydraulic press (SPECAC 15.011) using a pressure of 7 MPa, a processing temperature of 180 and 190 °C, respectively, and different periods of heat treatment, varying from 5 to 600 s. After pressing, the films were quenched in air at ambient temperature. The films were then annealed for 32 h at 75 °C, and finally the samples for mechanical investigations (s. Fig. 1) were cut from the films.

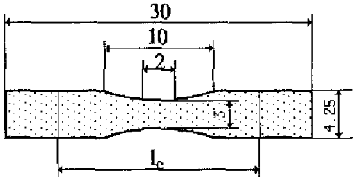

Figure 1 Sample for stress-strain measurements; dimensions in mm (l_c: distance between clamps = 20 mm).

The samples with a typical thickness of 70 µm were conditioned at constant temperature (T= 60 °C) and low humidity before testing. The crosshead velocity was 0,2 mm/min and the testing temperature about 23 °C.

RESULTS AND DISCUSSION

Figures 2 and 3 show the tensile strength as a function of the duration of heat treatment at different processing temperatures. Each measured value of tensile strength as well as Young's modulus were averaged from at least five tests.

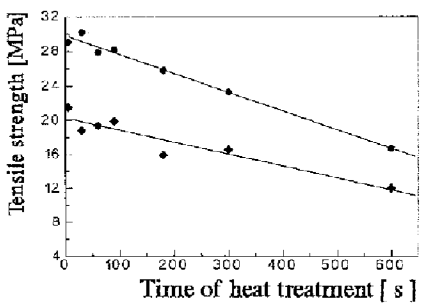

Figure 2 Tensile strength of P(3HB) ● and P(3HB-co-5mol%3HV) ◆ in dependence on time of heat treatment at 180°C.

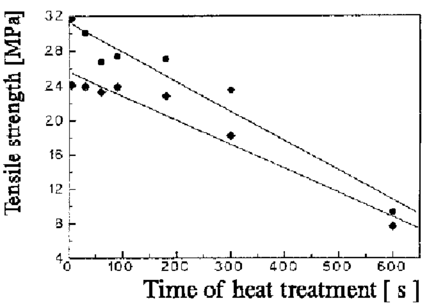

Figure 3 Tensile strength of P(3HB) ● and P(3HB-co-5mol%3HV) ◆ in dependence on time of heat treatment at 190°C.

In a first approximation, the straight lines in the diagrams represent the supposed linear dependence of tensile strength on time of heat treatment. The same approximation has been used in the following two diagrams in which the dependence of Young's modulus on time of heat treatment is shown.

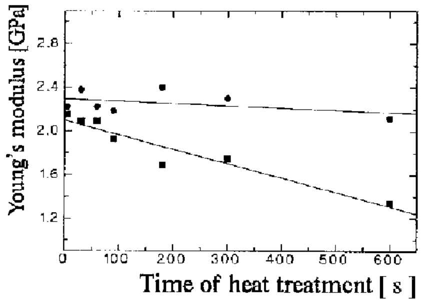

Figure 4 Young's modulus of P(3HB) ● and P(3HB-co-5mol%3HV) ■ in dependence on time of heat treatment at 180°C.

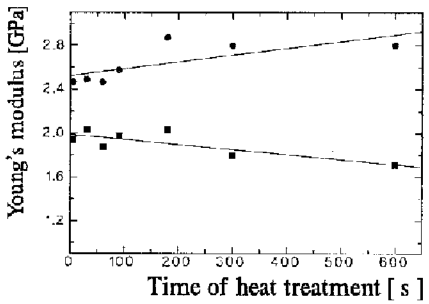

Figure 5 Young's modulus of P(3HB) ● and P(3HB-co-5mol%3HV) ■ in dependence on time of heat treatment at 190°C.

Figures 2 and 3 prove that the tensile strength strongly depends both on time and temperature of heat treatment. It is also obvious that the P(3HB) homopolymer exhibits a stronger decrease of tensile strength than the copolymer. After 10 minutes of thermal treatment at 190 °C the tensile strength of P(3HB) is reduced to one third of its initial value. This observation correlates with the results of GPC measurements which proved a decrease of molar mass with increasing time and temperature of heat treatment (s. Table 1).

Young's modulus depends only slightly on the time and temperature of heat treatment. While for P(3HB) the modulus is almost independent of time, for P(3HB-co-5mol%3HV) this quantity decreases slightly with time of heat treatment. This effect may be due to differences in crystallization and morphology caused by decreasing chain length of the macromolecules (s. Table 1).

Table 1 Results of GPC measurements of P(3HB-co-5mol%3HV) (average of 3 values)

Temperature of treatment	Time of treatment	M_n *10^{-3}	M_w *10^{-3}	M_w/M_n
[°C]	[s]	[g/mol]	[g/mol]	
As received		180	320	1,78
180	180	137	221	1,61
180	600	78	136	1,75
180	1200	57	82	1,45
190	300	41	67	1,63
190	1200	12	23	1,82

In Table 2 the values of the slope of the straight lines in Figures 3 to 6 are compiled which are characterized by the dimension [MPa/s] for tensile strength and [GPa/s] for Young's modulus, respectively. The calculated correlation coefficients prove that the measured values are represented by straight lines in a sufficient approximation.

Table 2 Slope of tensile strength and Young's modulus in dependence on time.

	Temperature of treatment	Slope of tensile strength	Correlation coefficient a)	Slope of Young's modulus	Correlation coefficient a)
Material	[°C]	[MPa/s]		[GPa/s]	
P(3HB)	180	-0,021	-0,99	-0,22	-0,43
P(3HB-co-3HV)	180	-0,014	-0,94	-1,35	-0,95
P(3HB)	190	-0,034	-0,97	0,62	0,73
P(3HB-co-3HV)	190	-0,028	-0,98	-0,46	-0,80

a) for the straight lines in Figures 3 to 6

Table 3 Constant k_d of thermal degradation according to equation [1] for P(3HB-co-5mol%3HV)

Temperature of treatment	k_d [as measured]	k_d [Kunioka and Doi /7/]
[°C]	[1/min]	[1/min]
180	$4{,}5 * 10^{-5}$	$3{,}8 * 10^{-5}$
190	$3{,}1 * 10^{-4}$	$1{,}4 * 10^{-4}$

In general, the measured constants of thermal degradation confirm the values recently published by Kunioka and Doi /7/ who reported that the constant k_d depends only on the temperature of heat treatment, but not on the chemical structure of PHB homopolymer or copolymer.

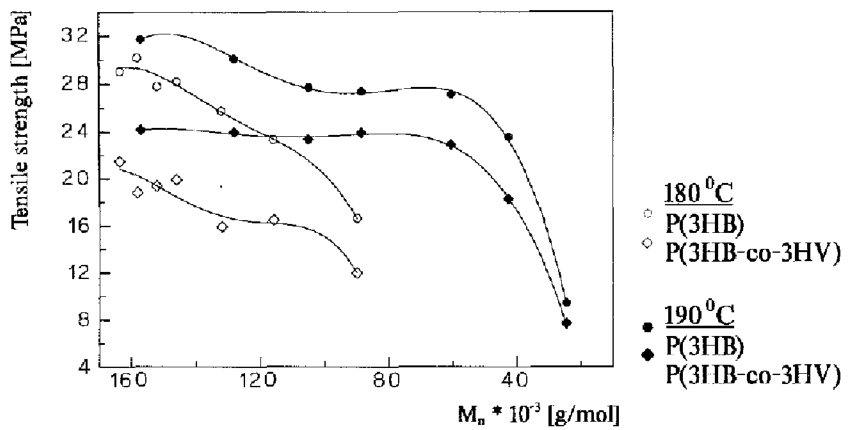

Figure 6 Tensile strength of P(3HB) and P(3HB-co-5mol%3HV) at 180 and 190 °C in dependence on number average of molar mass.

As shown in Figure 6 the tensile strength depends on the type of the polymer, the temperature of the heat treatment and the number average of molar mass. Again we suppose that the tensile strength is influenced by the morphology of the semicrystalline polymer. Higher temperature of the melt as well as lower molar mass of the polymer lead to a lower number of intrinsic nuclei for crystallization and hence to a lower number of spherulites with greater diameter. As reported by Holmes /1/ cracks are formed in the spherulites in PHB when the diameter reaches a critical value. These cracks lead to an embrittlement of the specimen and to lower tensile strength.

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