Supporting Information

Plasticization of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with an oligomeric polyester: Miscibility and effect of the microstructure and plasticizer distribution on the thermal and mechanical properties.

Jacqueline L. Barbosa, Giovanni B. Perin, Maria Isabel Felisberti[*]

Institute of Chemistry, University of Campinas, P.O. BOX: 6154, 13083-970, Campinas - SP, Brazil

Table of contents

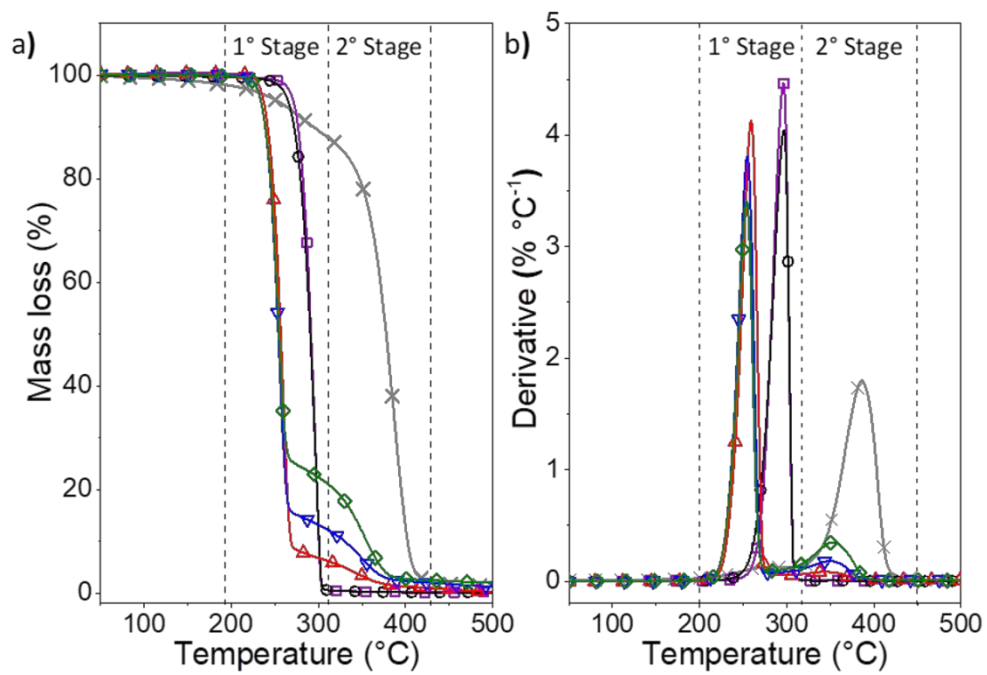1. Thermogravimetric curves and their derivative curves

Figure S1: a) TGA curves and b) derivative curves for unprocessed PHBV (□) and PLAP (x), and for the processed PHBV (○) and its formulations with PLAP mass fractions of 0.1 (△), 0.2 (▽) and 0.3 (◇).

2. Deconvolution of DMA curves

The E" *vs* T curves deconvoluted by Gaussian curves are presented in Figure S2.

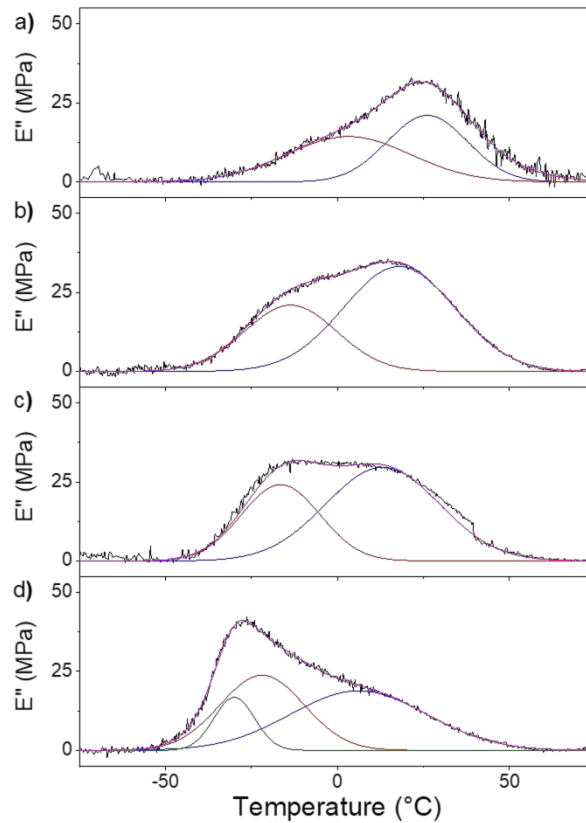Figure S2: E" *vs* T curves (black line) and their Gaussians for a) pure PHBV and its formulations with PLAP mass fractions of b) 0.1, c) 0.2, and d) 0.3.

The deconvolution of the tan δ *vs* T and E" *vs* T curves using Gaussians allows for the determination of the T_g of the rigid and mobile amorphous phases as the temperatures corresponding to the maximums of the Gaussians, which are summarized in Table S1 and S2.

Table S1: T_g and PHB and PLAP mass fraction in the rigid, mobile, and PLA-rich mobile amorphous phases determined from the deconvoluted tan δ *vs* T curves for PHBV and its formulations with PLAP mass fractions of 0.1, 0.2, and 0.3.

	Rigid amorphous phase			Mobile amorphous phase			PLAP-rich mobile amorphous phase		
w_{PLAP}	$T_{g,}$ (°C)	w_{PHBV}	w_{PLAP}	T_g (°C)	w_{PHBV}	w_{PLAP}	T_g (°C)	w_{PHBV}	w_{PLAP}
0.0	28	1.00	0.00	3	1.00	0.00	---	---	---
0.1	24	0.94	0.06	-8	0.71	0.29	---	---	---
0.2	22	0.91	0.09	-10	0.66	0.34	---	---	---
0.3	12	0.77	0.23	-10	0.64	0.36	-27.0	0.13	0.87

Table S2: T_g and PHB and PLAP mass fraction in the rigid, mobile and PLA-rich mobile amorphous phases determined from the deconvoluted E" *vs* T curves for PHBV and its formulations with PLAP mass fractions of 0.1, 0.2, and 0.3.

	Rigid amorphous phase			Mobile amorphous phase			PLAP-rich mobile amorphous phase		
w_{PLAP}	$T_{g,}$ (°C)	w_{PHBV}	w_{PLAP}	T_g (°C)	w_{PHBV}	w_{PLAP}	T_g (°C)	w_{PHBV}	w_{PLAP}
0.0	26	1.00	0.00	3	1.00	0.00	---	---	---
0.1	18	0.88	0.12	-14	0.53	0.47	---	---	---
0.2	13	0.80	0.20	-16	0.46	0.54	---	---	---
0.3	6	0.70	0.30	-22	0.30	0.70	-30	0.04	0.96

3. Estimation of the PLAP composition in amorphous phases

The PLAP mass fractions in the mobile and rigid amorphous phases were graphically estimated from the T_g of the mobile and rigid amorphous phases for pure PHBV (determined from tan δ vs T and E" vs T curves) and for PLAP (determined by DSC). The composition-dependence of the T_g of the mobile and rigid amorphous phases were plotted by using the Fox equation[76] (Equation S1), assuming that it adequately describes the dependence of T_g on the formulations composition, and presented in Figure S3.

$$\frac{1}{T_g} = \frac{w_{PHBV}}{T_{g,PHBV}} + \frac{(1 - w_{PHBV})}{T_{g,PLAP}} \qquad \text{Equation S1}$$

where $T_{g,\,PHBV}$, $T_{g,\,PLAP}$, and T_g are the glass transition temperatures of the pure PHBV, pure PLAP, and of the mobile or rigid amorphous phase, respectively.
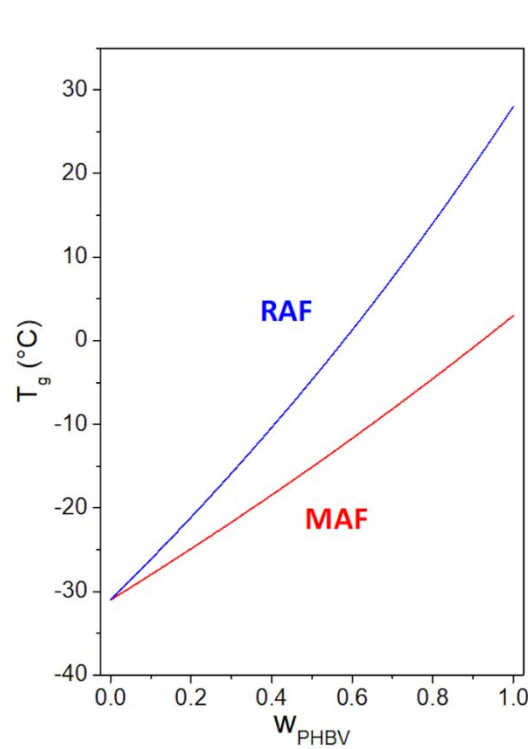

Figure S3: T_g of the mobile (-) and rigid (-) amorphous phases as a function of the PHBV mass fraction in the formulations with PLAP predicted by the Fox equation.

The compositions of each amorphous phase in the PHBV formulations (determined from tan vs T and E" vs T curves) are presented in Tables S1 and S2, respectively. The T_g of each phase and the PHBV and PLAP mass fraction (w_i) in each phase (i) for pure PHBV and its plasticized formulations (determined using data from E" vs T curves) are presented in Figure 4S.
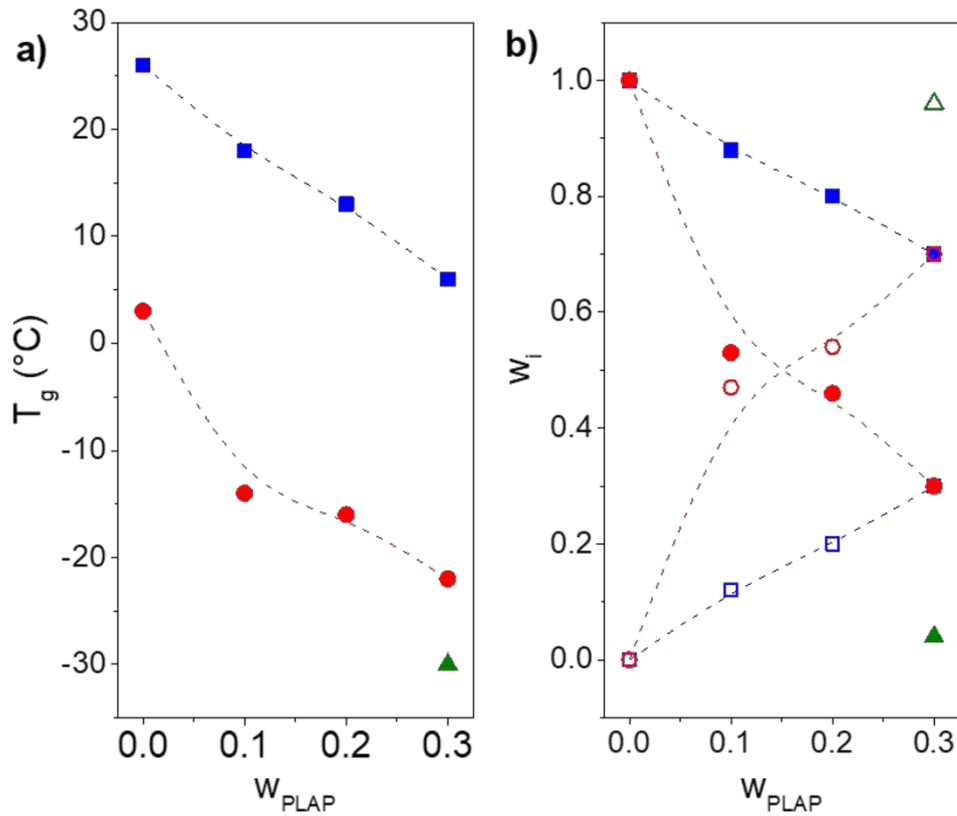

Figure S4: a) T_g and b) the PHBV (closed symbols) and PLAP (open symbols) mass fraction in the amorphous phases as a function of the PLAP mass fraction in the formulations: rigid (■,□), mobile (●,○), and PLAP-rich mobile amorphous phases (▲,△). Data determined from E" vs T curves.

4. SAXS analysis

The Lorentz corrected SAXS for aged and recrystallized samples of processed PHBV and its formulations with PLAP are presented in Figure S5.

Figure S5: Lorentz-corrected $I(q)q^2$ vs q curves for a) aged and b) recrystallized PHBV (-) and its formulations with PLAP mass fractions of 0.1 (-), 0.2 (-), and 0.3 (-).

The long period (L_p), the crystalline lamella (l_c), and the amorphous layer (l_a) were determined by using SAXDAT software. Based on the lamellar stack model of the polymer structure the morphological parameters were calculated using a correlation function as an inverse Fourier transform of the intensity distribution function.[73] From the correlation function, the thickness of the two phases (crystalline and amorphous) was determined, and the attribution of each phase was performed by comparing the volumetric degree of crystallinity of the formulation (Φ_c, equation S2) with the linear degree of crystallinity within the lamellar stacks (ϕ_c^{lin}, equation S3):[74]

$$\Phi c = \frac{\raisebox{0.5ex}{χ_c}\big/\raisebox{-0.5ex}{ρ_c}}{\raisebox{0.5ex}{χ_c}\big/\raisebox{-0.5ex}{ρ_{c-PHBV}} + \raisebox{0.5ex}{$(w_{PHB} - \chi_c)$}\big/\raisebox{-0.5ex}{ρ_a} + \raisebox{0.5ex}{w_{PLAP}}\big/\raisebox{-0.5ex}{ρ_{PLAP}}}$$

Equation S2

where χ_c is the degree of crystallinity measured by DSC, ρ_c and ρ_a are the densities of 100% crystalline PHB (ρ_c = 1.26 g cm^{-3}) and completely amorphous PHB (ρ_c = 1.18 g cm^{-3})[4], ρ_{PLAP} is the PLAP density (ρ_{PLAP} = 1.18 g cm^{-3}, determined by using a pycnometer), and w_{PHBV} and w_{PLAP} are the PHBV and PLAP mass fraction in the formulations.

$$\emptyset_c^{lin} = \raisebox{0.5ex}{l_c}\big/\raisebox{-0.5ex}{L_p}$$

Equation S3

The correlation functions for aged and recrystallized samples for processed PHBV and its formulations with PLAP are presented in Figure S6.

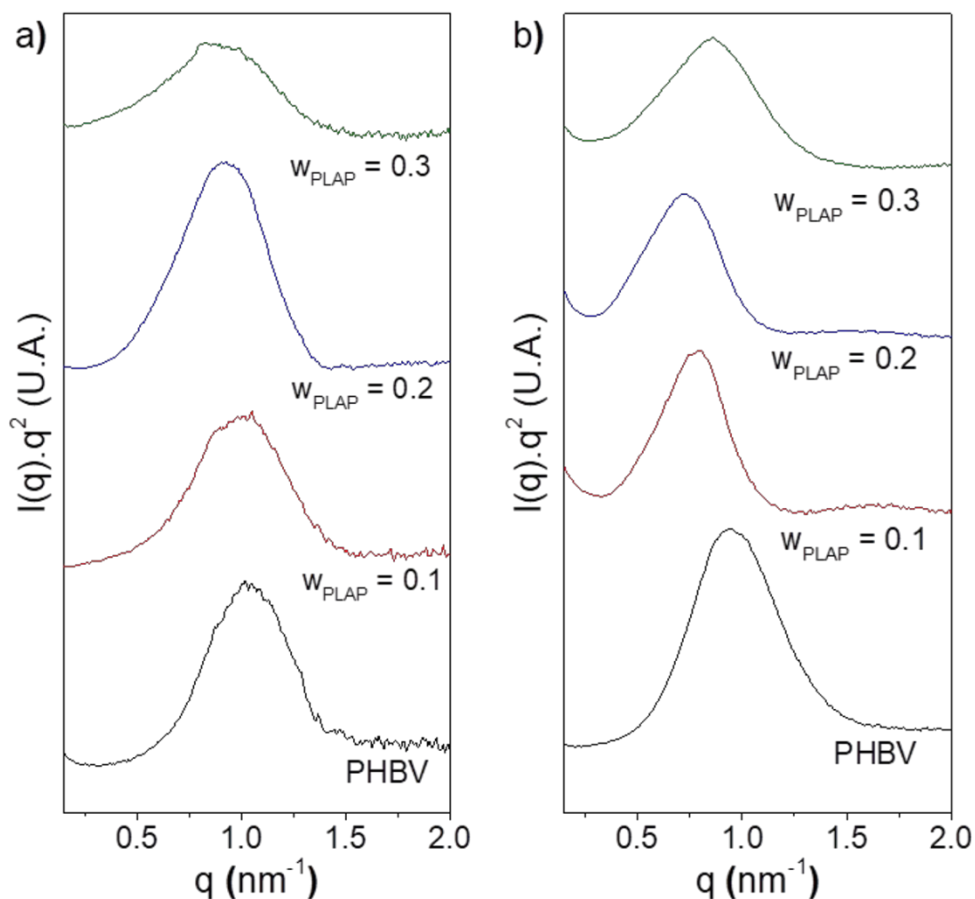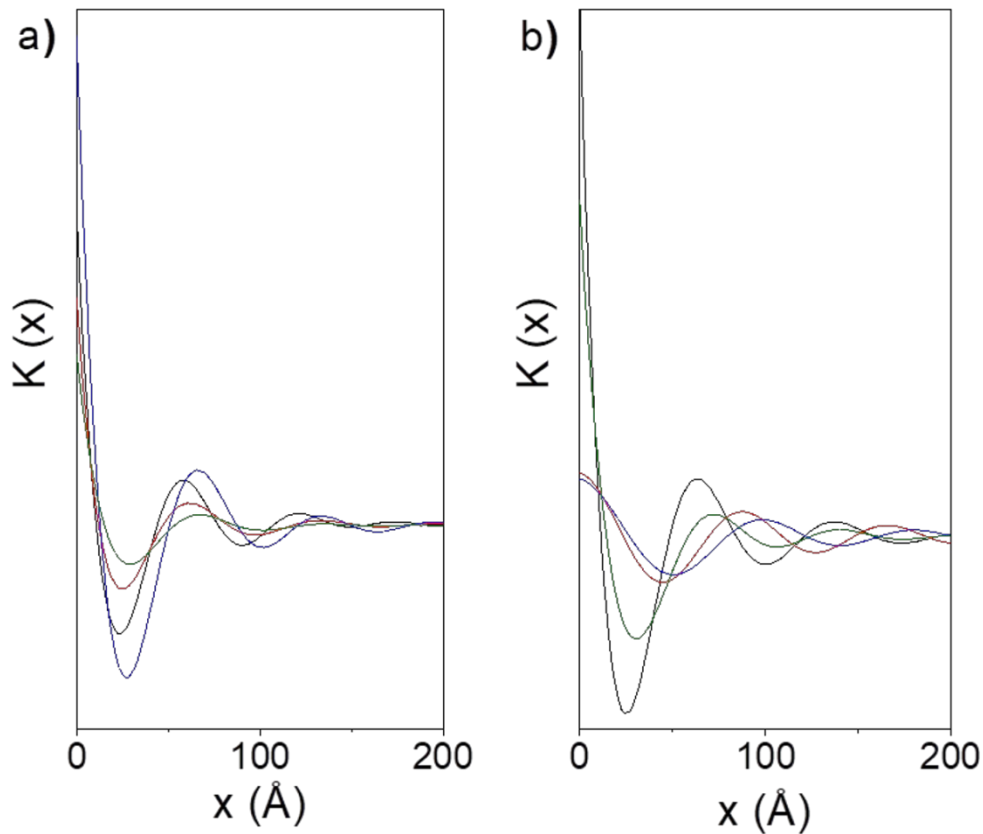Figure S6: Correlation functions for a) aged and b) recrystallized samples for processed PHBV (-) and its formulations with PLAP mass fractions of 0.1 (-), 0.2 (-), and 0.3 (-).

The structural parameters determined by SAXS are summarized in Table S3.

Table S3: Scattering vector at the peak maximum (q_{max}), long period (L_p), crystalline lamellae and amorphous layers thickness (l_c and l_a, respectively), linear degree of crystallinity within the lamellar stacks (ϕ_c^{lin}), and the volumetric degree of crystallinity (Φ_c) for aged specimens and thin films freshly crystallized at 70°C for 1 h.

	Aged specimens						Films freshly crystallized at 70°C for 1 h					
w_{PLAP}	q_{max} (nm^{-1})	L_p (nm)	l_c (nm)	l_a (nm)	Φ_c	ϕ_c^{lin}	q_{max} (nm^{-1})	L_p (nm)	l_c (nm)	l_a (nm)	Φ_c	ϕ_c^{lin}
0.0	1.03	5.8	4.4	1.4	0.53	0.76	0.94	6.2	4.7	1.5	0.56	0.76
0.1	0.99	6.1	4.7	1.4	0.55	0.77	0.78	8.7	5.1	3.6	0.51	0.58
0.2	0.92	6.5	4.8	1.7	0.56	0.75	0.72	9.8	5.7	4.1	0.46	0.58
0.3	0.89	6.7	4.9	1.8	0.60	0.72	0.86	7.3	5.4	1.9	0.41	0.75

5. Digital images of the spherulites

Digital images of unprocessed PHBV, processed PHBV, and its formulations with PLAP isothermally crystallized at 55, 65, and 75 °C are presented in Figure S7.
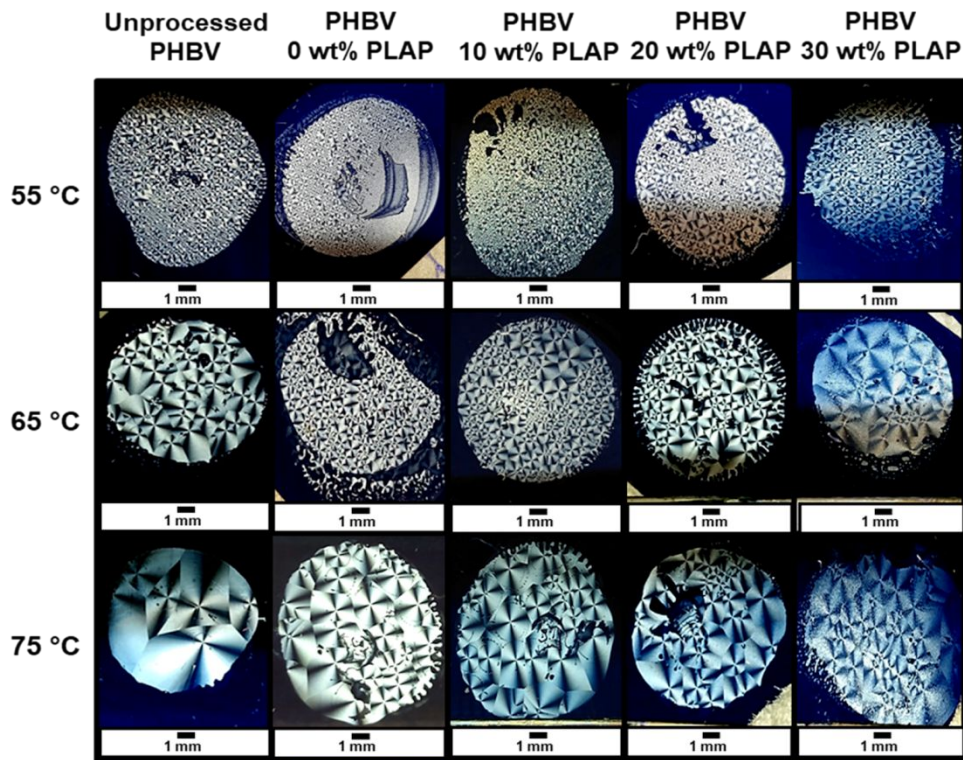

Figure S7: Digital images of unprocessed PHBV, processed PHBV, and its formulations with PLAP isothermally crystallized at 55, 65, and 75 °C.

6. Determination of the Flory-Huggins interaction parameter

The depression in the melting point of the plasticized PHBV was investigated according to the Flory-Huggins theory and the Nishi-Wang equation[68] (Equation 4):

$$\left(\frac{1}{T'_m} - \frac{1}{T^o_m}\right) = -\left(\frac{RV_{2u}}{\Delta H_{2u}V_{1u}}\right) * \left[\left(\frac{ln\emptyset_2}{Dp_2}\right) + \left(\frac{1}{Dp_2} - \frac{1}{Dp_1}\right)\emptyset_1 + \chi_{12}\emptyset_1^2\right]$$ Equation S4

where, T'_m and T^o_m are the melting temperatures of the plasticized and pure PHBV, respectively. Subscript 1 denotes the plasticizer PLAP and subscript 2 the PHBV. V_u is the molar volume of the mers, ΔH_u is the enthalpy of melting per mole of mers, Dp is the degree of polymerization, R is the universal gas constant, $\emptyset$ is the volume fraction, and $\chi_{1,2}$ is the Flory-Huggins interaction parameter. Rearranging equation S4 gives the following:

$$-\left[\left(\frac{\Delta H_{2u}V_{1u}}{RV_{2u}}\right)\left(\frac{1}{T'_m} - \frac{1}{T^o_m}\right)\right] - \left(\frac{ln\emptyset_2}{Dp_2}\right) - \left(\frac{1}{Dp_2} - \frac{1}{Dp_1}\right)\emptyset_1 = \beta = \chi_{1,2}\emptyset_1^2$$ Equation S5

$\chi_{1,2}$ is the slope of the curve of β as a function of $\emptyset^2_1$ (Figure S8).
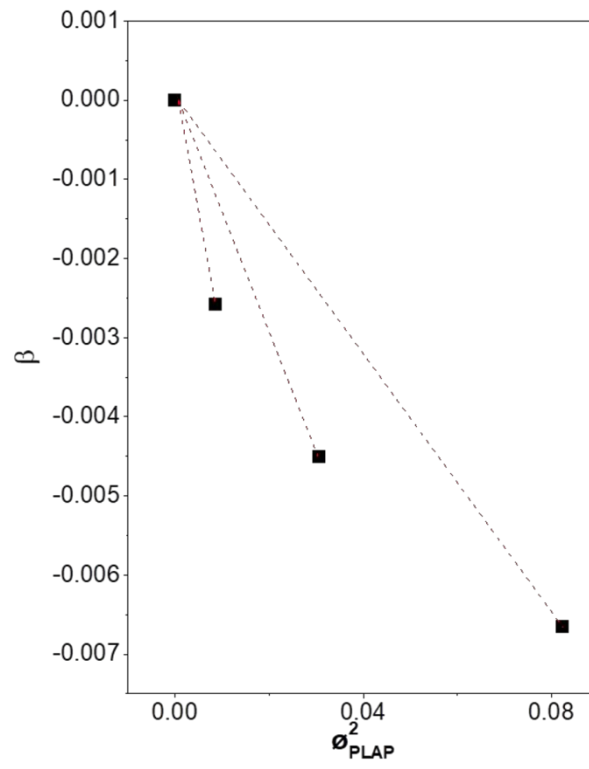
Figure S8: Plot of β vs φ^2_{PLAP} according to Equation S5.

7. Mechanical properties

Table S4 summarizes the results from the Izod impact resistance and tensile test analysis.

Table S4: Izod impact resistance, elastic modulus, tensile strength, and elongation at break for the specimens of PHBV and its formulations with PLAP mass fractions of 0.1, 0.2, and 0.3.

w_{PLAP}	Izod Impact Resistance (J m^{-1})	Elastic Modulus (MPa)	Tensile Strength (MPa)	Strain at Break (%)
0.0	96 ± 10	586 ± 28	30.5 ± 1.4	8.0 ± 0.0
0.1	130 ± 20	502 ± 16	26.3 ± 0.3	8.2 ± 0.4
0.2	224 ± 60	428 ± 35	22.2 ± 1.2	8.1 ± 0.4
0.3	212 ± 40	381 ± 22	18.9 ± 0.4	6.6 ± 0.5

10. Efficiency of plasticizers – a short review

To compare our data with data from literature for low molar mass and oligomeric plasticizers for PHB and PHBV, we choose the following parameters:

1. Depression of T_g expressed as

$$\Delta T_g = T_{g(Formulation)} - T_{g(Matrix)} \quad (°C) \quad \text{Equation S6}$$

2. Depression of T_m expressed as

$$\Delta T_m = T_{m(Formulation)} - T_{m(Matrix)} \quad (°C) \quad \text{Equation S7}$$

3. Percent change in the elastic modulus, E, expressed as

$$\Delta E = \left(\frac{E_{(Formulation)} - E_{(Matrix)}}{E_{(Matrix)}} \right) \times 100 \quad \text{Equation S8}$$

4. Percent change in the elongation at break, ε, expressed as

$$\Delta \varepsilon = \varepsilon_{Formulation} - \varepsilon_{Matrix} \quad \text{Equation S9}$$

These data for oligomeric and molecular plasticized PHB and PHBV are compiled in Tables S5 and S6, respectively.

Table S5: Efficiency of oligomeric plasticizers for decreasing T_g and T_m and for tuning the mechanical properties of the PHB and PHBV formulations.

Matrix	Plasticizer	Mass fraction	ΔT_g (°C)	ΔT_m (°C)	ΔE (%)	$\Delta \varepsilon$ (%)	Reference
PHBV (3% HV, M_w = 250 kDa)	PLAP (M_w = 6.5 kDa)	0.1	-3	-1	-14	0.2	this work
PHBV (3% HV, M_w = 250 kDa)	PLAP (M_w = 6.5 kDa)	0.2	-6	-2	-27	0.1	this work
PHBV (3% HV, M_w = 250 kDa)	PLAP (M_w = 6.5 kDa)	0.3	-11	-3	-35	-1.4	this work
PHBV (3% HV, M_w = 250 kDa)	PEG1000	0.1	n.d.	-1	-37	0.8	24
PHBV (3% HV, M_w = 250 kDa)	PEG1000	0.2	n.d.	0	-28	0.2	24
PHB	Poly(adipate) (M_n= 3.8 kDa)	0.1	-9	-4	-25	-0.2	32
PHB	Poly(adipate) (M_n= 3.8 kDa)	0.2	-17	-5	-43	1.8	32
PHB	Poly(adipate) (M_n= 3.8 kDa)	0.3	-32	-7	-53	3.5	32
PHBV (8% HV)	PEG200	0.1	0,0	-5	-14	0.4	39
PHBV (8% HV)	PEG1000	0.1	0,0	-2	-31	0.8	39
PHBV (8% HV)	PEG4000	0.1	0,0	-2	-30	0.3	39
PHBV (3% HV)	PEG400	0.1	-15	-6	-56	4.0	45
PHBV (3% HV)	PEG1000	0.1	n.d.	-4	-37	2.7	45
PHBV (3% HV)	PEG4000	0.1	n.d.	-2	-48	2.8	45
PHB (M_w = 600 kDa)	Poly[di(ethyleneglycol) adipate] (M_n= 2.5 kDa)	0.1	-10	-1	0	0.0	46
PHB (M_w = 600 kDa)	Poly[di(ethyleneglycol) adipate] (M_n= 2.5 kDa)	0.2	-13	-2	-25	0.0	46
PHB (M_w = 600 kDa)	Poly[di(ethyleneglycol) adipate] (M_n= 2.5 kDa)	0.3	-15	-2	-28	1.0	46
PHB	PEG4000	0.1	n.d.	-5	-36	-0.2	47
PHB	PEG6000	0.1	n.d.	-3	-27	0.7	47
PHB (M_n = 190 kDa)	PEG300	0.1	-15	-3	n.d.	7.0	49
PHB (M_n = 190 kDa)	Laprol 503	0.1	-13	-1	n.d.	7.0	49
PHB (M_n = 190 kDa)	Laprol 5003 (M_n= 5.0 kDa)	0.1	-1	2	n.d.	7.0	49
PHB (M_n = 190 kDa)	PHB (M_w = 3.6 kDa)	0.1	n.d.	0	-22	-0.9	63
PHB (M_n = 190 kDa)	PHB (M_w = 3.6 kDa)	0.2	n.d.	0	-12	-3.3	63
PHB (M_n = 190 kDa)	PHB-diol (M_w = 1.8 kDa)	0.2	-12	-11	n.d.	3.0	64
PHB	atactic PHB (M_n = 0.6 kDa)	0.1	-30	-4	n.d.	n.d.	65
PHB	atactic PHB (M_n = 0.6 kDa)	0.3	-52	-8	n.d.	n.d.	65
PHB	atactic PHB (M_n = 2.7 kDa)	0.1	-18	-2	n.d.	n.d.	65
PHB	atactic PHB (M_n = 2.7 kDa)	0.3	-23	-6	n.d.	n.d.	65
PHB	medium-chain-length PHA (M_n = 4.6 kDa)	0.1	n.d.	-0,9	-38	-5.0	66
PHB	medium-chain-length PHA (M_n = 4.6 kDa)	0.2	n.d.	-7,6	-62	2.0	66

Continuation of Table S5.

Matrix	Plasticizer	Mass fraction	ΔT_g (°C)	ΔT_m (°C)	ΔE (%)	$\Delta \varepsilon$ (%)	Reference
PHB (M_w = 370 kDa)	Pluronic F68 (M_w = 8.4 kDa)	0.2	-10	-2	20	-12,6	67
PHB (M_w = 370 kDa)	Pluronic F127 (M_w = 12.6 kDa)	0.2	-10	-3	n.d.	n.d.	67
PHBV (5% HV, M_n = 300 kDa)	Poly(caprolactone)-triol	0.1	-11	-2	n.d.	n.d.	69
PHBV (5% HV, M_n = 300 kDa)	Poly(caprolactone)-triol	0.2	-12	-6	n.d.	n.d.	69
PHBV (5% HV, M_n = 300 kDa)	Poly(caprolactone)-triol	0.3	-12	-8	n.d.	n.d.	69
PHB (ENMAT Y1000)	Tolonate X FLO100	0.1	n.d.	0	-1	2.0	70
PHB (ENMAT Y1000)	Tolonate X FLO100	0.2	n.d.	-1	-20	4.0	70

n.d. – not determined.

Table S6: Efficiency of low molar mass plasticizers for decreasing T_g and T_m and for tuning the mechanical properties of PHB and PHBV.

Matrix	Plasticizer	Mass fraction	ΔT_g (°C)	ΔT_m (°C)	ΔE (%)	$\Delta \varepsilon$ (%)	Reference
PHB (M_n = 330 kDa)	Dioctyl sebacate	0.3	-10	-5	-75	1,8	31
PHB (M_n = 330 kDa)	Acetyl tributyl citrate	0.1	-16	-6	-9	3,6	31
PHB (M_n = 330 kDa)	Acetyl tributyl citrate	0.2	-35	-9	-55	6,0	31
PHB (M_n = 330 kDa)	Acetyl tributyl citrate	0.3	-37	-12	-87	7,2	31
PHB	Dioctyl phthalate	0.1	-9,5	-5	-39	3,5	32
PHB	Dioctyl phthalate	0.2	-10,1	-6	-51	3,1	32
PHB	Dioctyl phthalate	0.3	-11,5	-9	-63	1,6	32
PHB	Dioctyl adipate	0.1	-7,7	-3	-18	-1,3	32
PHB	Dioctyl adipate	0.2	-7,6	-6	-37	-0,8	32
PHB	Dioctyl adipate	0.3	-7,5	-6	-39	-2,7	32
PHB	Triacetyl glycerol	0.1	-10,4	-6	-43	0,4	32
PHB	Triacetyl glycerol	0.2	-17,4	-11	-74	3,3	32
PHB (M_w = 800 kDa)	Salicylic acid decyl ester	0.3	-38	n.d.	-72	102,0	35
PHB (M_w = 800 kDa)	Salicylic acid 2-butyloctyl ester	0.3	-38	n.d.	-73	20,0	35
PHB (M_w = 800 kDa)	Acetylsalicylic acid hexyl ester	0.3	-24	n.d.	-77	124,0	35
PHB (M_w = 800 kDa)	Acetylsalicylic acid dexyl ester	0.3	-17	n.d.	-72	32,0	35
PHB (M_w = 800 kDa)	Ketoprofen ethyl ester	0.3	-24	n.d.	-80	56,0	35
PHB (M_w = 800 kDa)	Triethyl citrate	0.3	-34	n.d.	-68	19,0	35
PHB (M_w = 800 kDa)	Butyryltrihexyl citrate	0.3	-33	n.d.	-73	30,0	35
PHBV (8% HV)	Lauric acid	0.1	0	-5	-11	0,1	39
PHBV (8% HV)	Stearic acid	0.1	0	-8	-22	-0,7	39
PHB (M_w = 670 kDa)	Glycerol triacetate	0.2	-23,5	-13,2	-58	59	43
PHB (M_w = 670 kDa)	Glycerol tripropionate	0.2	-30,3	-12,8	-41	5	43
PHB (M_w = 670 kDa)	Glycerol tributyrate	0.2	-30,8	-12,1	-61	21	43
PHB (M_w = 670 kDa)	Glycerol tricapronate	0.2	-20,6	-6,3	-49	17	43
PHB (M_w = 670 kDa)	Glycerol tricaprylate	0.2	-16,3	-4,2	-53	32	43
PHB (M_w = 670 kDa)	Glycerol trilaurate	0.2	-2,4	-0,2	-60	4	43
PHB (M_w = 670 kDa)	Glycerol tripalmitate	0.2	-1,4	-1,1	-34	-1	43
PHB (M_w = 670 kDa)	Glycerol tristearate	0.2	-3,2	-0,3	-18	-3	43
PHB (M_w = 670 kDa)	Glycerol diacetate	0.2	-25,9	-11,2	-23	14	43
PHB (M_w = 670 kDa)	Glycerol dilaurate	0.2	-18,7	-5,7	-21	-2	43
PHB (M_w = 670 kDa)	Glycerol monoacetate	0.2	-1,8	-11,9	-26	-3	43
PHB (M_w = 670 kDa)	Glycerol monolaurate	0.2	-6,6	-12,9	-53	0	43
PHB (M_w = 670 kDa)	Glycerol monostearate	0.2	-23,6	-14,7	-49	15	43

Continuation of Table S6.

Matrix	Plasticizer	Mass fraction	ΔT_g (°C)	ΔT_m (°C)	ΔE (%)	$\Delta \varepsilon$ (%)	Reference
PHB (M_w = 600 kDa)	Glyceryl tributyrate	0.1	-5	-1	0	1,0	46
PHB (M_w = 600 kDa)	Glyceryl tributyrate	0.2	-5	0	-13	2,0	46
PHB (M_w = 600 kDa)	Glyceryl tributyrate	0.3	-10	-2	-16	6,0	46
PHB	Acetyl tributyl citrate	0.1	n.d.	-6	-36	2,2	47
PHB	Epoxidized soybean oil	0.1	n.d.	-4	-23	1,8	47
PHB (M_n = 190 kDa)	Dibutyl sebacate	0.1	-13	-5	n.d.	7,0	49
PHB (M_n = 190 kDa)	Dioctyl sebacate	0.1	-5	-2	n.d.	7,0	49
PHB (M_n = 460 kDa)	Maleinized linseed oil	0.1	-1,4	-3,8	-15	0,8	52
PHB (M_n = 460 kDa)	Maleinized linseed oil	0.2	-1,2	-4,6	-17	-1,5	52
PHB (M_n = 460 kDa)	Octyl epoxy sterate	0.1	0,5	-3,4	-23	3,1	52
PHB (M_n = 460 kDa)	Octyl epoxy sterate	0.2	0,5	-3,9	-23	1,8	52
PHBV (6% HV)	Soybean oil	0.1	1	-3	-22	-1	54
PHBV (6% HV)	Soybean oil	0.2	2	1	-18	-1,9	54
PHBV (6% HV)	Soybean oil	0.3	3	-2	-20	-2,4	54
PHBV (6% HV)	Epoxidized soybean oil	0.1	-2	-1	-33	1,6	54
PHBV (6% HV)	Epoxidized soybean oil	0.2	-12	-1	-43	1,9	54
PHBV (6% HV)	Epoxidized soybean oil	0.3	-14	-1	-56	2,2	54
PHB	Geraniol	0.1	-13	-7	-42	2,9	57
PHB	Geraniol	0.2	-20	-8	-62	3,1	57
PHB	Linalool	0.1	-11	-6	-44	3,0	57
PHB	Linalool	0.2	-18	-3	-48	3,8	57
PHB	Geraniol acetate	0.1	-17	-6	-52	5,3	57
PHB	Geraniol acetate	0.2	-22	-12	-73	11,7	57
PHB (M_w = 397 kDa)	Triethyl citrate	0.1	-10	-6	-20	-0,2	75
PHB (M_w = 397 kDa)	Triethyl citrate	0.2	-25	-10	-44	1,6	75
PHB (M_w = 397 kDa)	Triethyl citrate	0.3	-29	-18	-63	1,1	75

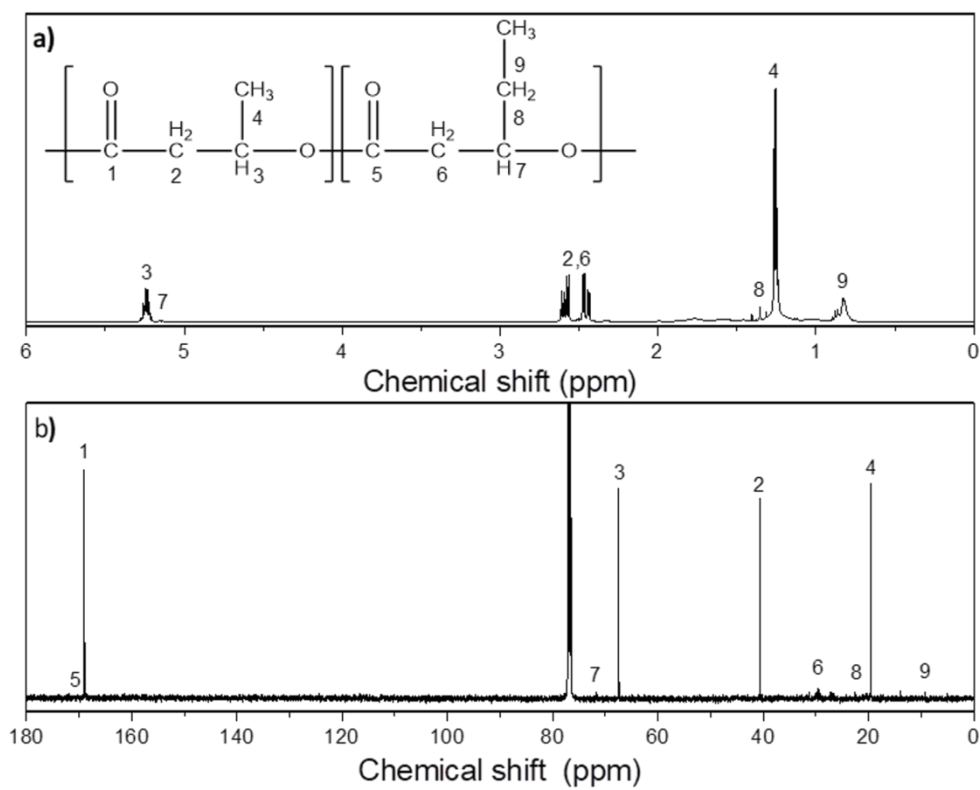n.d. – not determined.

8. ^{1}H and ^{13}C NMR spectra of PHBV

Figure S9: a) ^{1}H and b) ^{13}C NMR spectra of pure PHBV in CDCl$_3$.
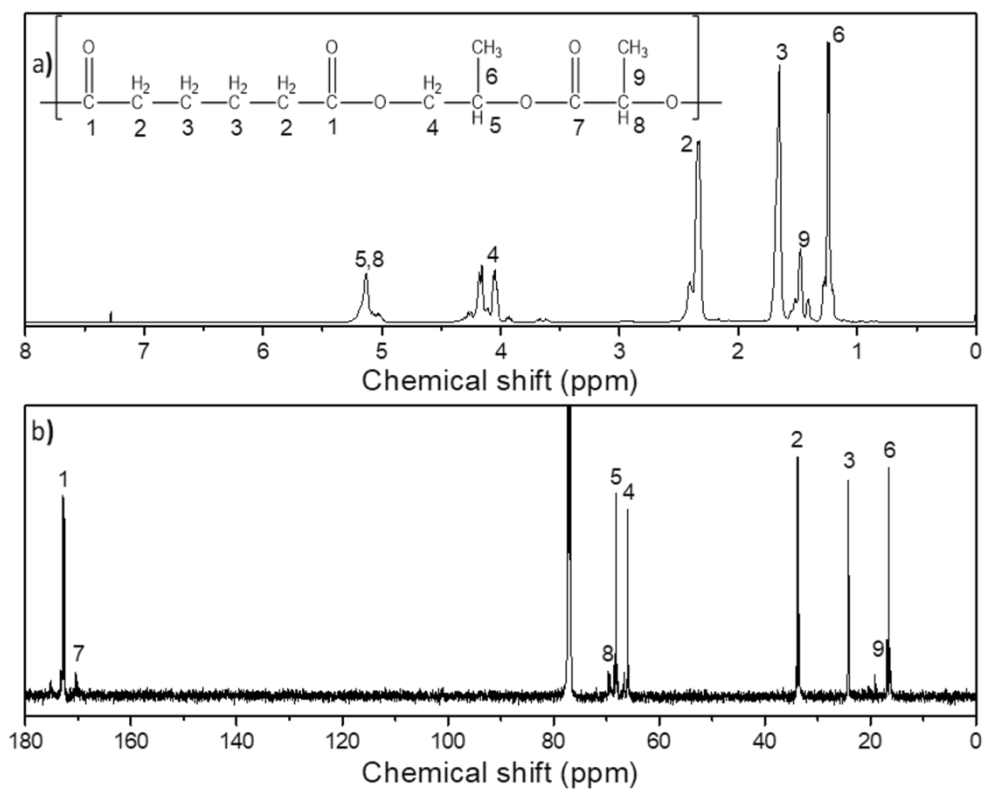
9. ¹H and ¹³C NMR spectra of PLAP

Figure S10: a) ¹H and b) ¹³C NMR spectra of pure PLAP in CDCl₃.