

Solubility factors as screening tools of biodegradable toughening agents of polylactide

Alexandre Ruellan, Alain Guinault, Cyrille Sollogoub, Violette Ducruet,

Sandra Domenek

► To cite this version:

Alexandre Ruellan, Alain Guinault, Cyrille Sollogoub, Violette Ducruet, Sandra Domenek. Solubility factors as screening tools of biodegradable toughening agents of polylactide. Journal of Applied Polymer Science, 2015, 132 (48), 10.1002/APP.42476. hal-01269141

HAL Id: hal-01269141 https://hal.science/hal-01269141

Submitted on 3 Jan 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Solubility factors as screening tools of biodegradable toughening agents of polylactide

Alexandre Ruellan,^{1,2,3} Alain Guinault,^{1,4} Cyrille Sollogoub,^{1,4} Violette Ducruet,⁵ Sandra Domenek²

¹Laboratoire Procédés et Ingénierie en Mécanique et Matériaux, Arts et Métiers ParisTech, 21 Rue Pinel, F-75013, Paris, France ²Unité Mixte de Recherche 1145 Ingénierie Procédés Aliments, AgroParisTech, 1 Avenue des Olympiades F-91300, Massy, France

³Département R&D, Brodart Packaging, 1 Rue du Stand, F-10700, Arcis-Sur-Aube, France

⁴Laboratoire Propriétés et Architectures des Alliages et Mélanges, CNAM, 2 Rue Conté, F-75003, Paris, France

⁵Unité Mixte de Recherche 1145 Ingénierie Procédés Aliments, INRA, 1 Avenue des Olympiades, F-91300 Massy, France

Correspondence to: Sandra Domenek (E-mail: sandra.domenek@agroparistech.fr)

ABSTRACT: Changes in the thermomechanical properties of polylactide (PLA) plasticized by two biodegradable and biobased molecules, Polysorb ID37 (PID37) and squalene, were compared to formulations with petroleum-based plasticizers, namely, acetyl tributyl citrate, poly(ethylene glycol) 400, and dioctyl adipate (DOA). The solubility parameters of the additives were calculated and were related to the plasticization behaviors. PID37 proved to be miscible with PLA because of its polar functions and short alkyl groups. It decreased the PLA glass-transition temperature (T_g) and increased in ductility when T_g approached room temperature. Squalene had a low miscibility because of the absence of polar groups. T_g was not depressed. Ductility improvements were nevertheless reached because the immiscible inclusions efficiently induced crazing by the distribution of stress concentration points all over the material; this delayed failure. The maximum elongations at break were 60% for squalene, 400% for DOA, and 500% for PID37. The solubility factors were, thus, an efficient prediction tool for the plasticizing behavior.

KEYWORDS: biodegradable; biopolymers and renewable polymers; mechanical properties; packaging; plasticizer

INTRODUCTION

For almost 2 decades, new polymers have been developed with the aim of lowering the environmental impact of plastics manufacturing. Polylactide (PLA), which is a biobased and compostable polyester produced on a large scale, exhibits numerous advantages, including a glass-transition temperature (T_g) that is higher than room temperature, ease of processing, high transparency, printability, and moderate cost. However, even if PLA offers satisfying mechanical properties, its low deformation at break remains a limitation for many high-volume applications, such as textile fiber production and food packaging.^{1,2}

External plasticizing is a widely applied method for enhancing polymer ductility because of existing know-how and the ease of implementation of such a process on the industrial scale. Many studies have been conducted to find effective PLA plasticizers. Plasticizers should be high-boiling-point molecules, miscible with the polymer, having a high associated free volume and low T_{g} . For polar polymers such as polyesters, plasticizer molecules should have polar groups acting as points of interaction to ensure good compatibility and nonpolar groups (as alkyl chains) masking the neighboring polymer chain dipoles and increasing the free volume.³

As plasticizers are often used in compounds at concentrations of up to 30 wt %, it is interesting that they are biodegradable and biobased if such claims are envisaged to be associated with the polymer. Additives derived from biomass byproducts have already been shown to enhance the ductility of PLA. Miscibility has been observed to be a key factor. In fact, merely miscible glucose monoester and fatty acid esters,⁴ glycerol,⁵ liquefied rice bran,⁶ α -tocopherol, and resveratrol⁷ did not induce significant T_g decreases nor improvements in the elongation at break. In contrast, oligomeric lactic acid,⁵ liquefied wood,⁶ and limonene⁸ caused large decreases in the PLA T_g concomitantly with gains in the ductility. To enhance the compatibility with PLA, chemically modified biomass fractions, such as epoxidized soybean oil^{1,9,10} and epoxidized palm oil,^{11–13} have been tested.



Figure 1. Chemical structures of the PLA and plasticizers.

Improvements in the elongation at break were obtained,^{9,11–14} whereas the PLA glass-transition merely decreased.

To produce competitive plasticizers, the performance of biobased plasticizers need at least to approach that of one of the petrochemical molecules. Among petroleum-based plasticizers that have already been investigated, citrate esters^{15–22} are the far most prominent ones. Labrecque *et al.*²² mixed triethyl citrate, tributyl citrate, acetyl triethyl citrate, and acetyl tributyl citrate (ATBC) at a concentration of 20 wt % with PLA. In all cases, T_g was lowered, and the elongation at break augmented to 300%. Poly(ethylene glycol)s (PEGs) have also attracted large interest, mainly because they are commercially available in a large range of chain lengths. It has been observed that smallchain-length PEG [weight-average molecular weight $(M_w) < 1000$]^{15,21,23,24} tends to induce stronger thermomechanical changes than those with longer chain lengths.^{15,25–27} Furthermore, adipate esters, which have two polar functions, have been studied as PLA plasticizers.^{17,28,29} Martino *et al.*²⁹ used dioctyl adipate (DOA) up to a concentration of 20 wt % and successfully increased the elongation at break to approximately 300%.

In this study, we examined two fully biobased and biodegradable molecules as new plasticizers for PLA. Polysorb ID37 (PID37) is an isosorbide diester recently developed by the Roquette Group; at first, it was intended for the lamination of poly(vinyl chloride), but it is potentially usable as a PLA plasticizer.^{30,31} The isosorbide core is derived from glucose and prepared from the double dehydration of sorbitol, and the ester alkyl chains are sourced from vegetable oils. PID37 was recently registered in the European Union Regulation Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). The second potential plasticizer, squalene, is a common natural hydrocarbon extracted from vegetables or shark liver. Its main uses are in cosmetics, food supplements, and adjuvants of vaccines.

With an aim to probe the effects of those molecules on PLA ductility and to investigate the corresponding plasticizing mechanisms, we compounded amorphous PLA with PID37 and squalene and compared the properties to those of known

Table I. Processing Conditions for Blend Compounding by Twin-Screw Extrusion

			Screw rotation	PLA 4060D feeding	Additive feeding
Formulation		Temperature profile (°C)	speed (rpm)	input (kg/h)	input (kg/h)
Neat PLA		175/180/190/190/190/190/180	300	0.620	_
PLA +	5 wt % ATBC	175/180/180/180/180/180/170	300	0.600	0.031
	10 wt % ATBC	175/180/170/170/165/160/160	300	0.600	0.072
	15 wt % ATBC	175/175/170/165/160/155/155	300	0.550	0.098
	20 wt % ATBC	175/170/160/160/160/150/150	300	0.550	0.136
PLA +	5 wt % PEG 400	175/180/180/175/175/170/170	300	0.600	0.032
	10 wt % PEG 400	175/175/170/170/170/170/165	300	0.600	0.075
	15 wt % PEG 400	170/170/170/165/160/155/150	300	0.600	0.107
	20 wt % PEG 400	170/170/165/160/155/150/150	300	0.600	0.150
PLA +	5 wt % DOA	175/180/180/180/190/180/175	300	0.620	0.033
	10 wt % DOA	175/175/175/180/180/175/170	300	0.620	0.070
	15 wt % DOA	175/175/175/180/180/175/170	300	0.620	0.108
	20 wt % DOA	175/175/175/180/180/175/170	300	0.620	0.154
PLA +	5 wt % PID37	170/180/175/175/170/170/170	300	0.580	0.030
	10 wt % PID37	170/180/170/165/165/165/160	300	0.580	0.066
	15 wt % PID37	170/180/170/160/160/160/155	300	0.580	0.104
	20 wt % PID37	170/180/170/160/155/150/150	300	0.580	0.147
PLA +	5 wt % squalene	175/180/180/170/170/170/165	300	0.610	0.034
	10 wt % squalene	175/180/170/170/170/170/165	300	0.610	0.070
	15 wt % squalene	175/180/170/170/170/170/165	300	0.610	0.104
	20 wt % squalene	175/180/170/170/170/170/165	300	0.610	0.149

Table II. Molar Constants for the Calculation of the Solubility Values Obtained from Ref. 32

	F _d	F _p ²	E _h	Molar volume					
Group	(J ^{1/2} cm ^{-3/2} mol ⁻¹)	(J cm ⁻³ mol ⁻¹)	(J/mol)	(cm ³ /mol)	ATBC	PEG 400	DOA	PID37	Squalene
>C<	-70	0	0	-19.2	1	0	0	0	0
=C<	70	0	0	-5.5	0	0	0	0	6
>CH-	80	0	0	-1.0	0	0	0	4	0
=CH-	200	0	0	13.5	0	0	0	0	6
-CH2-	270	0	0	16.1	11	16-18	18	10-18	10
-CH3	420	0	0	33.5	4	0	2	2	8
-COO-	390	240,100	7000	18	4	0	2	2	0
-OH	210	250,000	20,000	10	0	2	0	0	0
-0-	100	160,000	3000	3.8	0	7-8	0	2	0
Ring	190	0	0	16	0	0	0	2	0
One plane of symmetry	_	Total $ imes$ 0.50	_	_	0	0	1	0	1

 F_{dr} dispersion contribution; F_{pr} polar contribution; E_{hr} hydrogen-bonding-energy contribution.

petrochemical plasticizers having similar molecular weights. Two different mechanisms of PLA ductility increases were observed as a function of the plasticizer solubility. The first one was linked to the decrease in T_g by the plasticizer, and the second one was linked to the induction of crazing.

EXPERIMENTAL

Materials

PLA 4060D, with a D-lactic acid content of $11 \pm 1\%$ (according to the datasheet), was purchased from NatureWorks. ATBC, poly(ethylene glycol) 400 (PEG 400), DOA, and squalene were supplied by Sigma-Aldrich (France). PID37 was provided by the Roquette Group (France). Chemical structures of the plasticizers are shown in Figure 1. Before compounding, the PLA pellets and plasticizers were dried at 60°C for 24 h under dried air to remove water traces with an SOMOS 60L. The relative humidity of dried pellets was controlled to be lower than 350 ppm with an Aboni FMX HydroTracer.

Neat PLA and plasticized PLA sheets were prepared in two successive steps. First, the direct melt-mixing of additives with PLA was carried out with a corotating twin-screw extruder (Thermo Haake Ptw 16-40D) with a screw diameter of 16 mm and a length-todiameter ratio of 40 : 1. Blends of PLA containing 5, 10, 15, and 20 wt % of each plasticizer were prepared. The liquid addition of each plasticizer was performed in the third of seven zones of the extruder. The processing conditions are given in Table I. After cooling under air, the strand was pelletized. The obtained pellets were stored in hermetic metalized sealed bags to prevent rehydration. Second, the different PLA compounds were thermomolded (Laboratory Press Gibitre Instruments, 20 tons). The pellets were premelted at 180°C without pressure for 180 s, and then, the heated plates of the press were closed with a progressive increase in pressure up to 220 bar for 120 s to eliminate air bubbles. The obtained sheets were then cooled to ambient temperature by air. The thickness of the sheets was approximately 1 mm.

Characterization of the PLA Films

To quantify the amount of plasticizer added to PLA, around 6 g of the formulated pellets were placed into a 125-mL Soxhlet apparatus containing 200 mL of ethanol and extracted under reflux for 8 h. Then, the extracted PLA pellets were dried for 2 days at 40°C *in vacuo*. We measured the weight content of the plasticizer by weighing the difference of the PLA pellets. Analyses were done in duplicate.

The average molecular weight and dispersity values of the neat and formulated PLA sheets were measured by size exclusion chromatography with a Waters Co. apparatus equipped with an isocratic pump (GILSON 307), a column oven (Waters Control Module II), a gel column (Styragel H5E 7.8 \times 300 mm²) having a separation range from 2000 to 1000,000 g/mol, an autosampler (Waters 717 plus), and a refractive index detector (Waters 2414). Data acquisition and analysis were carried out with the help of Breeze Software. The analyses were performed at 35°C with tetrahydrofuran as an eluent at a flow rate of 1 mL/min. The calibration was done before the experiments with polystyrene standards (Shodex Standard from Showa Denko, range = 3070–778,000 g/ mol). For sample preparation, neat and formulated PLA pellets were dissolved in tetrahydrofuran (20 mg/L) on a shaker at 60°C for 45 min. The analyses were done in triplicate.

The thermal analyses were carried out with a Mettler Toledo DSC1 STARe System under a nitrogen atmosphere (50 mL/min). The calibration of the device was done with pure water and an indium standard before the experiments. Samples of around 7 mg were cut from the thermomolded sheets and put into hermetic aluminum pans (40 μ L). For each sample, calorimetric scans were carried out at a heating/cooling rate of 10°C/min. Thermal history was suppressed by heating from 0 to 70°C (first scan), and this was followed by an isotherm at 70°C for 5 min. Then, the samples were cooled down from 70 to -40° C (second scan); subsequently, a heating scan from -40 to 100°C (third scan) was performed. T_g

Formulation	Targeted plasticizer content (wt %)	Extracted plasticizer content (wt %)	M _n (a/mol)	M _w (a/mol)	Dispersitv
Nonextruded PLA	_	_	104.500 + 2300	244.500 + 4100	2.34 + 0.01
PIA + ATBC	0	_	79 300 + 4500	209 600 + 5400	2.64 ± 0.09
	5	4.2 ± 0.3	88.000 ± 2900	211.700 ± 3900	2.41 ± 0.04
	10	8.9±0.4	88.100 ± 3500	210.900 ± 7000	2.39 ± 0.02
	15	13.9 ± 0.4	93,900 ± 4300	, 221,800 ± 4400	2.36 ± 0.06
	20	17.8±0.6	90,600 ± 2200	, 217,100 ± 2700	2.40 ± 0.03
PLA + PEG 400	0	_	83,600 ± 1900	214,100 ± 6300	2.56 ± 0.02
	5	4.9 ± 0.4	76,600 ± 2600	181,100 ± 7500	2.36 ± 0.02
	10	10.8 ± 0.6	73,900 ± 3400	165,900 ± 8900	2.24 ± 0.02
	15	14.4 ± 0.2	69,100 ± 4100	157,300 ± 5800	2.28 ± 0.05
	20	18.3 ± 0.4	61,800 ± 2400	128,300 ± 8900	2.08 ± 0.07
PLA + DOA	0	_	81,200 ± 2700	$211,400 \pm 4400$	2.60 ± 0.03
	5	4.7±0.2	93,700 ± 2400	209,400 ± 7500	2.23 ± 0.02
	10	8.8±0.1	94,500 ± 2400	207,600 ± 2100	2.20 ± 0.03
	15	12.9 ± 0.7	90,600 ± 1200	$204,100 \pm 4000$	2.25 ± 0.01
	20	17.2 ± 0.5	$91,900 \pm 3200$	208,600 ± 8100	2.27 ± 0.01
PLA + PID37	0	-	85,100 ± 3600	$208,400 \pm 7100$	2.45 ± 0.02
	5	4.3 ± 0.4	$81,400 \pm 4100$	$210,900 \pm 3800$	2.59 ± 0.09
	10	9.8 ± 0.0	82,200 ± 2800	$207,300 \pm 4200$	2.52 ± 0.04
	15	14.4 ± 0.2	$80,300 \pm 1900$	$202,000 \pm 1900$	2.52 ± 0.04
	20	18.8 ± 0.6	79,600 ± 6500	$199,900 \pm 7900$	2.51 ± 0.12
PLA + squalene	0	—	85,300 ± 2600	$206,600 \pm 4900$	$2,\!42\pm0.02$
	5	3.7 ± 0.3	$86,500 \pm 1900$	$202,400 \pm 5300$	2.34 ± 0.01
	10	7.1 ± 0.2	$91,300 \pm 3200$	$202,100 \pm 2800$	2.21 ± 0.05
	15	9.9 ± 0.1	90,200 ± 2700	$205,600 \pm 3300$	2.28 ± 0.03
	20	11.9 ± 0.6	87,600 ± 1400	200,800 ± 6300	2.29 ± 0.04

Table III. Extracted Plasticizer Contents, Molar Weight Averages, and Dispersities of the PLA/Plasticizer Formulations

was taken at the midpoint of the heat capacity step in the third scan. The experiments were done in triplicate.

The plasticizer T_g was determined at the midpoint of the heat capacity step with a heating scan from -95 to 25° C at a heating rate of 2° C/min. The experiments were carried out in duplicate.

The tensile properties were investigated at 23° C, at $50 \pm 10\%$ relative humidity, and at a crosshead speed of 25 mm/min with a universal tensile machine (Instron model 4301). Dog-bone samples (ISO 527-2, type 5A) were cut from the thermomolded sheets. Before tensile testing, the samples were conditioned at 23° C and $50 \pm 10\%$ relative humidity for at least 72 h. The thickness of the samples varied from 0.9 to 1.1 mm. Each given value was an average of 10 measurements.

The morphologies of the samples before and after the tensile tests were observed with scanning electron microscopy (Hitachi 4800 II). Observations were done directly on the surface of the dog-bone-shaped samples without any previous preparation.

Calculation of the Solubility Parameters

The molar volumes and molar interaction constants of the PLA and plasticizers were determined according to the van Krevelen and Hoftyzer atomic group contribution method. Tables can be found in van Krevelen *et al.*'s work.³² Because the length of the PID37 alkyl ester chains is unknown, calculations were done with a saturated alkyl chain length between 6 and 10 carbons. Because PEG 400 is an oligomer with an average molar mass between 380 and 420 g/mol (according to the data sheet), calculations were done with degrees of polymerization ($n_{\rm f}$ s) of 6 and 7.

The average molar volumes $[V_g(T)$'s; cm³/mol] at 25°C of the amorphous and glassy chains of PLA were estimated with eqs. (1) and (2). According to size exclusion chromatography measurements [number-average molecular weight $(M_n) = 104,200$ g/mol], the average n_i was about 1450. With amorphous molar volume increment values at 298 K,³² the van der Waal's volume of the repeating lactide unit $(F_{ij} \text{ cm}^3/\text{mol})$ was estimated to 55.72 cm³/mol:

$$V_g(T) = F(1.30 + 0.55 \times 10^{-3} T_g + 0.45 \times 10^{-3} T)$$
(1)

$$F = \sum n_i F_i \tag{2}$$

where *F* is the van der Waal's volume of the polymer chain (cm^3/mol) , *T* is room temperature (K), and n_i the polymerization degree of the molar chain.³³

	I								
Substance	M _w (a/mol)	Molar volume (cm ³ /mol)	T ₂ (°C)		Ť	ISP		HiSI	
			ש	δ_d (J ^{1/2} cm ^{-3/2})	$\delta_{ m p}$ (J ^{1/2} cm $^{-3/2}$)	δ_h (J ^{1/2} cm ^{-3/2})	RED	δ (J ^{1/2} cm ^{-3/2})	Difference
PLA	244,500	130,500	57	18.6 ^b	9.9 ^b	6.0 ^b	$(radius = 10.7)^{b}$	21.9	
ATBC	402	364	-83.2	16.9	2.7	7.6	0.76	18.7	3.2
PEG 400	370-414	304-340	-66.2	17.9	4.2-4.0	14.2-13.7	0.94-0.91	23.2-22.9	1.3-1.0
DOA	370	393	-104^{a}	16.5	0.0	6.0	0.93	17.6	4.3
PID37	342-454	300-428	-80.8	17.4-17.2	3.0-2.1	8.2-6.8	0.71-0.78	19.5-18.6	2.4-3.3
Squalene	410	477	-75.3	16.1	0	0	1.18	16.1	5.8
^a According to re ^b According to re	эf. 57. эf. 36.								

Table IV. Physical Data and Computed Solubility Parameters for PLA and Plasticizers

The Hansen solubility parameters (HSPs) of each plasticizer were calculated with eqs. (3)-(5).^{34,35} The used molar constants³² are presented in Table II. However, the estimation of HSP of very long chain polymers such as PLA 4060D with only the group contribution method is not reliable enough because the three-dimensional configuration is not considered. Therefore, we used literature values obtained by computed calculations and published by Abbott:³⁶

$$\delta_d = \frac{\sum F_{di}}{\sum V_i} \tag{3}$$

$$\delta_p = \frac{\sqrt{\sum F_{P_i}^2}}{\sum V_i} \tag{4}$$

$$\delta_h = \sqrt{\frac{\sum E_{hi}}{\sum V_i}} \tag{5}$$

where δ_d is the dispersion component of the solubility parameter (J^{1/2} cm^{-3/2}), δ_p is the polar component of the solubility parameter (J^{1/2} cm^{-3/2}), δ_h is the hydrogen-bonding component of the solubility parameter (J^{1/2} cm^{-3/2}), F_{di} is the dispersion contribution of the molar attraction constant [(J^{1/2} cm^{-3/2})/mol⁻¹], F_{pi} is the polar contribution of the molar attraction constant [(J^{1/2} cm^{-3/2})/mol⁻¹], E_{hi} is the hydrogen-bonding-energy contribution of the molar attraction constant (J/mol), and V is the molar volume contribution of the chemical group involved (cm³/mol).

The solubility of the five molecules in PLA was assessed with the HSP relative energy difference (RED) from eqs. (6) and (7):

Distance=
$$\sqrt{4(\delta_{dplast} - \delta_{dPLA})^2 + (\delta_{pplast} - \delta_{pPLA})^2 + (\delta_{hplast} - \delta_{hPLA})^2}$$
(6)

$$RED = \frac{Distance}{Radius}$$
(7)

where $\delta_{db} \delta_{pp}$ and δ_h are the components of the solubility parameters of the plasticizer obtained from eqs. (3), (4), and (5), respectively, and the ones of PLA obtained from Abbott.³⁶ The radius is the maximal distance³⁶ beyond which the additives are not miscible anymore with the polymer. Therefore, the closer the RED value is to zero, the better the compatibility is. An RED value higher than 1 indicates theoretical nonmiscibility of the plasticizer with the matrix.

A second method can be applied with the group contribution method [eq. (8)]. In this case, the Hildebrand solubility parameter (δ or HiSP), which is the outcome of HSP with eq. (9), is obtained. Cohesive energy values ($E_{\rm coh}$'s) can calculated as follows:³²

$$\delta = \sqrt{\frac{E_{\rm coh}}{V}} \tag{8}$$

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \tag{9}$$

where δ is the solubility parameter (J^{1/2} cm^{-3/2}).

The obtained value of the HiSP of PLA with eq. ((3).(8)) was 22.1 $J^{1/2}$ cm^{-3/2}; this was close to the value of 21.9 $J^{1/2}$ cm^{-3/2} determined with eq. (9) and HSP of PLA found in ref. 36.



Figure 2. Experimental T_g values of the PLA/plasticizer formulations plotted with the corresponding Fox equation (dashed lines): (a) ATBC, (b) PEG 400, (c) DOA, (d) PID37, and (e) squalene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Consequently, in this study, we found HSP of PLA from ref. 36 as suitable to be compared with the calculated HSP of plasticizers with the group contribution method.

The solubility of the five molecules in PLA was also assessed with HiSP. In this case, the numerical difference between HiSP of PLA and HiSP of the plasticizers was computed. The larger the value was, the lower the compatibility of the plasticizer with the matrix was.

RESULTS AND DISCUSSION

Analysis of the Plasticizer Content and Average Molecular Weight of Compounded PLA

The plasticizer incorporated in the compounds was quantified, and Table III shows a comparison of the measured concentrations with the target concentration. For ATBC, PEG 400, DOA, and PID37, the incorporated amounts were close to the target values; this indicated little additive loss during twin-screw extrusion. The squalene quantities were substantially smaller than the target amounts and showed a loss of the plasticizer during processing. Indeed, an accumulation of liquid squalene inside the twin-screw extruder was observed.

The average molecular weight of the PLA samples is also given in Table III. The blank PLA showed moderate thermal degradation of the macromolecular chain length during twin-screw extrusion. This decrease was linked to the high sensitivity of PLA to hydrolysis and/or the thermomechanical input.^{2,17,21} When ATBC, DOA, PID37, or squalene was added, the degradation was less important; this was likely due to the lower extrusion temperatures needed for plasticized PLA and/or to the internal lubrication, which reduces the shearing. In contrast, PEG 400 induced large decreases in both M_n and M_w . The decrease in the macromolecular chain length caused by the compounding of PLA with PEG was already largely described in the literature and explained by transesterification reactions between PLA and PEG.^{21,37}

Miscibility Study

The high D content of the PLA grade $(11 \pm 1\%)$ according to the datasheet) used in this study inhibited PLA crystallization. Generally, at D contents higher than 6%, PLA is amorphous under common experimental conditions.^{38,39} Therefore, compatibility between PLA and the different plasticizers was assessed with the help of HSP and HiSP, which are prediction methods adapted to amorphous polymers.³² The datasets are presented in Table II. The solubility prediction by the two methods was different. HiSP predicted the highest solubility for PEG, whereas HSP classified PID37 to be the most soluble. This difference was caused by the contribution of the hydrogen interaction, which is only taken into account in Hansen's method.³⁶ δ_h of PEG 400 was very far from that of PLA (Table IV) because of the absence of hydroxyl groups able to establish H bonds. ATBC and PID37 additives were predicted to be soluble in PLA



Figure 3. Typical stress/strain curves of the PLA/plasticizer formulations: (--) PLA + 5 wt % plasticizer, (--) PLA + 10 wt % plasticizer, (---) PLA + 15 wt % plasticizer, and (----) PLA + 20 wt % plasticizer. [Color figure can be viewed in the online issue, which is available at wileyon-linelibrary.com.]

according to HSP and HiSP. PEG 400 and DOA had nearly the same solubility in PLA after Hansen's method. On the contrary, squalene was predicted to be faintly soluble in PLA.

The prediction of the solubility was confirmed by the study of the miscibility and miscibility limits of the plasticizers through the measurement of the T_g decrease of compounded PLA and modeling with Fox's equation:

$$\frac{1}{T_g} = \frac{\omega_{\text{PLA}}}{T_g PLA} + \frac{\omega_{\text{Plast}}}{T_g Plast}$$
(10)

where T_g is the glass-transition temperature of the formulated material; T_{gPLA} and T_{gPlast} are the glass-transition temperatures of the neat PLA and the pure plasticizer, respectively; and ω_{PLA} and ω_{Plast} are the weight fractions of the neat PLA and plasticizer, respectively.

The results are presented in Figure 2. PID37 showed similar behavior to ATBC. Both molecules were miscible with PLA over the whole experimental concentration range; this was shown by the concordance between the experimental and predicted T_g values. With regard to PEG 400, the experimental values were slightly lower than the calculated ones, maybe because of a supplementary decrease in T_g caused by PLA chain scission during processing (Table III). A deviation of the T_g decrease from Fox's equation indicating the reaching of the miscibility limit was observed after 15 wt % PEG 400. This concentration was

smaller than the miscibility limit of the short PEGs $(M_w < 34,000 \text{ g/mol})$ established at 20 wt %^{15,40} and higher than the limit of 10 wt % observed in ref. 21 Squalene and DOA showed a leveling off of T_g at 48 and 41°C, respectively, despite the increase in the plasticizer content. The miscibility limit of DOA in PLA was reached at a concentration of 5 wt %; this was in accordance with Murariu *et al.*⁴¹ and the one of squalene at 3 wt %. These observations were in accordance with the prediction of low solubility by the HSP and HiSPs. Solubility theories are thus a valuable tool for screening biobased plasticizers.

Tensile Properties of the Plasticized PLA

Figure 3 shows typical results of the tensile testing of the PLA samples containing different plasticizers. The numerical data are given in Table V. Neat PLA showed brittle fracture at an elongation at break of about 5%, a behavior largely described in literature.^{17,22,24,29} The fracture mechanism of PLA glasses was crazing because of the low entanglement density.⁴² The blending with the different plasticizers induced the brittle-to-ductile transition. Two behavior groups could be distinguished; this was in accordance with the prediction of the solubility parameters.

PID37 was classified with ATBC and PEG 400 in the first behavior group. In that case, the brittle-to-ductile transition occurred when the plasticizer content was high enough to

Table V. Tensile Testing Results and T_g Data for the PLA/Plasticizer formulations

Formulation	Plasticizer content (wt %)	Elongation at break (%)	Apparent Young's modulus (MPa) ^a	Elongation at yield (%)	Stress at yield (MPa)	<i>T_g</i> (°C)
PLA + ATBC	0	4.8 ± 0.8	1660 ± 105	4.3±0.8	65 ± 5	56.1 ± 0.2
	4.2 ± 0.3	4.3 ± 0.3	1540 ± 90	3.9 ± 0.1	57 ± 5	45.9 ± 0.5
	8.9 ± 0.4	4.4 ± 0.4	1405 ± 125	4.0 ± 0.4	53 ± 5	37.9 ± 0.3
	13.9 ± 0.4	455 ± 125	270 ± 120	4.3 ± 0.8	7 ± 3	28.0 ± 0.8
	17.8 ± 0.6	505 ± 70	70 ± 20	4.5 ± 0.3	4 ± 1	21.6 ± 0.8
PLA + PEG 400	0	5.0 ± 0.3	1755 ± 170	4.4 ± 0.3	64 ± 2	56.0 ± 0.7
	4.9 ± 0.4	4.9 ± 0.7	1580 ± 135	4.2 ± 0.6	47 ± 6	41.8 ± 0.7
	10.8 ± 0.6	110± 80	1040 ± 80	4.8 ± 0.1	29 ± 4	30.5 ± 0.2
	14.4 ± 0.2	275 ± 35	740 ± 45	4.8 ± 0.2	16 ± 6	21.7 ± 0.4
	18.3 ± 0.4	135 ± 120	710 ± 65	4.6 ± 0.4	21 ± 4	22.2 ± 0.8
PLA + DOA	0	4.9 ± 0.9	1750 ± 100	4.0 ± 0.2	69 ± 3	57.4 ± 0.4
	4.7 ± 0.2	23 ± 7	1495 ± 60	2.9 ± 0.2	52 ± 5	42.5 ± 0.2
	8.8 ± 0.1	54 ± 13	1385 ± 15	2.6 ± 0.1	34 ± 1	41.1 ± 0.4
	12.9 ± 0.7	175 ± 40	1340 ± 40	2.4 ± 0.1	25 ± 3	40.9 ± 0.3
	17.2 ± 0.5	410 ± 10	1095 ± 60	2.3 ± 0.2	21 ± 1	40.7 ± 0.8
PLA + PID37	0	4.9 ± 0.9	1770 ± 60	3.9 ± 0.2	69 ± 3	56.2 ± 0.6
	4.3 ± 0.4	4.7 ± 0.5	1730 ± 40	3.6 ± 0.4	65 ± 3	46.2 ± 0.3
	9.8 ± 0.0	4.5 ± 0.9	1670 ± 45	3.2 ± 0.2	57 ± 3	40.4 ± 1.0
	14.4 ± 0.2	200 ± 25	915 ± 110	3.8 ± 0.2	20 ± 4	31.9 ± 0.5
	18.8 ± 0.6	530 ± 15	30 ± 20	3.5 ± 0.5	6 ± 4	22.4 ± 0.5
PLA + squalene	0	5.2 ± 0.4	1685 ± 85	4.3 ± 0.3	67 ± 4	56.2 ± 0.5
	3.7 ± 0.3	40 ± 5	1285 ± 70	3.2 ± 0.6	54 ± 5	50.9 ± 0.7
	7.1 ± 0.2	60 ± 10	1150 ± 20	3.1 ± 0.4	42 ± 5	49.4 ± 0.3
	9.9 ± 0.1	30 ± 10	1045 ± 55	2.8 ± 0.2	29 ± 6	48.9 ± 0.8
	11.9 ± 0.6	20 ± 10	1000 ± 110	2.5 ± 02	26 ± 4	48.0 ± 1.2

^a For comparison, this was obtained without an extensiometer.

depress T_g to the tensile testing temperature, more precisely when the onset of the glass-transition region was at 23°C. The PLA/ATBC mixtures showed no decrease in the stress at yield up to 10 wt % plasticizer, whereas beyond this value, plasticizing was very efficient. The curves lost the yield peak and showed plastic flow and hardening at high elongations due to

PLA	ATBC	PEG400	DOA	PID37	Squal
corem ipsum d liamcorper en ursus neo tinc (6, fingilla pia- passa and the possi ugue egot pur pontectetur me nonis tallus S titricise consec- tictum placerat em. Nam oma- sis, vitae vesti thedrum matiesue olupat sem, natesuada luct me molise tito.	lolor sit amet, consectetur, co, eu sodales velt. Dus idunt nec, conque vitae un cerart nist. Nem malesuad nean ut nulla sit amet sapi erer. Vivamus vitae blandi a. Quisque ut egestas oro sus varius s _{tab} lerfaque nec tus. Suspendisse mi velit de purus augue, dirpbus : utat sapien eget fingilla A. i aculis y vivamus eu sem rare euismod furpis, eget vo bulum justo lorem quis m sapien tortor, at dignisma. I ellura aliquam nunc fauci us, dui est vanicula dolor;	adipisoing elit, Curabitur adip eget justo eu veilt molestie na. Nuns sodielss condimenti turpis. Alquari di est findót i hulla phareta nula eget i sed erat. Pellenteque et cur adipiscing ut placerat ac. w adipiscing ut placerat ac. w adipiscing ut placerat ac. w adipiscing ut placerat ac. sodialis, tristique odi ut, susci prenatis magna vulputate nei sodialis, tristique odi ut, susci prenatis magna vulputate nei sodialistica di utori acisu vel portu uma massa eute diol	scing liber a nel san ornare a non cuu m eros sagitti retum deo, unt, vest ulur aftel, sus ligut fusce sen sus ligut fusce sen socialis at or 1 ero p sus ligut fusce sen to dois acculis at anet leo e convr s nibh Cras social Mot rus social Mot augue posure. Nu gait n tvelit nisi d turs met loren part turpis en s let ornare s let	us, ao dictum lectus acco m. Morbi eget orci odio. hr urtum ut. Maura nial e accurstam molestie. C. intee porta ante inferdum ullamos per tellus. Nulla harera i acculs runo, a p libero, commodo alquet partera i acculso in nectu s ao finadunt orci, ut sus t vehicula neque in lacre t vehicula neque in lacre s ao finadunt orci, ut sus t vehicula neque in lacre t vehicula neque in lacre	umsan. Ma c Fusce ligit a ligula, ormina a ac. Fusce à li im venenats, cu orona lacus. Co qui ell sit amet, e sportitor luco. Al sportitor luco. Al sportitor luco. sportitor luco. sportitor luco. sportitor gues escenas vel ve tat n, veli gues for m sec utpa for m sec utpa for no locen sasc fundos.

Figure 4. Picture of the PLA samples with plasticizers (15 wt %) after failure.

necking. This sudden change between 10 and 15 wt % ATBC was already shown.²¹ For ATBC, this most probably occurred only starting from this amount with enough free volume to the polymer to allow chain rearrangement. Molecules with branched nonpolar groups, such as ATBC, have the faculty to shield polymer dipoles and space polymer chains from each other. Softening is then mainly brought about by the added free volume of the branched molecule.43 Interestingly, PID37, which had a higher dispersive component (Table IV) but in sum had almost equal solubility parameters and molecular volumes, showed a more gradual behavior. A gain in elongation at break was observed at a concentration of 15 wt %. The highest value of the elongation at break observed was equal to that of ATBC plasticizing; this made PID37 an interesting biobased and biodegradable alternative to ATBC. Probably the long aliphatic chains of PID37 helped to reduce the polar interactions of the PLA chains and provide chain mobility at lower contents. The more gradual plasticizing behavior was also measured with PEG, which is a linear molecule. However, at high PEG contents, the elongation at break decreased again, likely because of phase separation as the miscibility limit was reached.^{23,44} This was consistent with the miscibility prediction by the analysis of the T_{g} ,



Figure 5. Scanning electron micrographs of the surface of the PLA samples with plasticizers (15 wt %) near the failure zone after failure.

shown in Figure 2. PEG phase separation induced flaws in the material, from which cracks started, and this induced consequence failure at lower elongations.^{23,44}

DOA and squalene compounds could be classified in the second behavior group. The materials reached high elongation at break values, whereas Tg of PLA remained higher than room temperature (Table V). Stress crazing is typical of brittle materials, whereas stress shearing enables high plasticity and ductile behavior.45 The transition between these two mechanisms is related, on the one hand, to the molecular entanglement density. A low entanglement density promotes crazing, whereas a high entanglement density causes shearing.⁴⁶⁻⁴⁸ The plasticizers DOA and squalene apparently did not bring enough free volume to the polymer to allow chain rearrangement under stretching because of their low miscibility. The T_g values of the DOA and squalene formulations were significantly higher than the tensile testing temperature. The ductility was, therefore, linked to cavitation and crazing. The crazes in the material appeared most likely from the matrix discontinuities created by the inclusion of additive droplets. The soluble quantity of the plasticizers could have enhanced chain slippage into the craze; this is needed for rapid fibril formation.^{48,49} The stress at yield level of the shear flow plateau decreased as a function of the plasticizer quantity. The occurrence of cavitation and fibril formation was observed by extensive stress whitening of both samples, a phenomenon that was not observed in the case of miscible molecules (Figure 4).

To illustrate the cavitation mechanism, scanning electron microscopy pictures of the surface of the stretched samples of PLA plus 15 wt % plasticizer until breakage were taken (Figure 5). For highly miscible molecules, that is, ATBC and PID37, no significant presence of the dispersed phase was observed. A few narrow cracks perpendicular to the stretching direction appeared. On the basis of the corresponding tensile curves, the strain hardening before ultimate rupture could have been caused by disentangled portions of the polymer. In the case of PEG 400, which was less soluble than ATBC or PID37 when the

results of the two solubility theories were averaged, some undissolved droplets of additives were observed. Although there were a few microcrazes, no stress whitening was observed. In the case of the DOA and squalene samples, an important quantity of the dispersed phase was seen, and the cavitation phenomenon evolved into bigger cracks, especially for the merely soluble squalene.

Even with immiscible plasticizers, the ductility of PLA could thus be improved. In a number of applications, the improvement in elongation at break observed in this study could be sufficient to meet requirements. The advantage of this mechanism is that the apparent Young's modulus remained high. However, one condition for applications is that stress whitening is not prohibitive. For example, the maximum elongation at break of the PLA/DOA mixtures reached 410%, which was higher than the one obtained with PEG 400 (Table V). The modification of the crack-propagation behavior and reduction of the brittleness during maintenance of the stiffness are typical effects of impact modifiers on PLA.⁵⁰⁻⁵⁵ According to NatureWorks, effective impact modifiers are rubbery compounds with a low T_g and crystallinity. Moreover, they are immiscible and dispersed in small domains in a glassy matrix and present good interfacial adhesion with PLA.56 Both DOA and squalene showed these characteristics. However, below 10 wt % DOA, Murariu et al.41 observed a decrease in the impact strength explained by the antiplasticization effect.

The difference between DOA and squalene could be anticipated with the help of the solubility factors, which showed that squalene was clearly outside of the solubility sphere of PLA, whereas DOA was just at the limit. The small part of miscible DOA molecules that lowered T_g could bring enough mobility to enhance chain slippage at the edges of the crazes, as proposed by Piorkowska *et al.*⁴⁴ Moreover, the slightly better miscibility of DOA likely allowed a more homogeneous distribution of the additive droplets in PLA. These differences might have been responsible for the higher elongation at break obtained with DOA compared to squalene. Indeed, a larger number of stress

concentration points ensures a better sharing of the mechanical energy during the stretching process; this delays the effective failure of the sample.⁴⁴

CONCLUSIONS

The plasticizing behaviors of the biobased molecules PID37 and squalene in PLA were discriminated with the help of their solubility factors. They provided a sound prediction of the possibility of a given molecule to lower T_{g^*} . If the additive miscibility in PLA was important, the ductility increased only when the PLA became rubbery at testing temperature. In consequence, a minimal amount of plasticizer was required, and the rigidity of the material is strongly depressed. In this case, PID37 was found to be an effective biobased and biodegradable plasticizer. If the plasticizer was merely miscible as in the case of squalene, the ductility could nevertheless be enhanced, whereas PLA remained in the glassy state by cavitational deformation. Furthermore, the efficient dispersion of nonmiscible inclusions allowed us to maintain the stiffness. Because moderate ductility is required in applications, squalene could constitute an interesting ecofriendly additive for PLA plasticization.

ACKNOWLEDGMENTS

This work was financially supported by Brodart Packaging and the Association Nationale Recherche Technologie (ANRT). It is part of the French project BIP-ADEME CREABioM, which is supported by the Agence de l'environnement et de la maîtrise de l'énergie (ADEME). The authors gratefully acknowledge the Roquette Group for the free supply of PID37 and, in particular, Vincent Berthe for his valuable help. They also thank Anne Grandmontagne and Cedric Plessis very much for their valuable technical support.

REFERENCES

- 1. Anderson, K. S.; Schreck, K. M.; Hillmyer, M. A. Polym. Rev. 2008, 48, 85.
- 2. Lim, L. T.; Auras, R.; Rubino, M. Prog. Polym. Sci. 2008, 33, 820.
- Ruellan, A.; Ducruet, V.; Domenek, S. Poly(lactic acid) Science and Technology: Processing, Properties, Additives and Applications; Royal Society of Chemistry: London, 2015; Chapter 5, p 124.
- 4. Jacobsen, S.; Fritz, H. G. Polym. Eng. Sci. 1999, 39, 1303.
- 5. Martin, O.; Averous, L. Polymer 2001, 42, 6209.
- 6. Azwar, E.; Yin, B.; Hakkarainen, M. J. Chem. Technol. Biotechnol. 2012, 88, 897.
- Hwang, S. W.; Shim, J. K.; Selke, S. E. M.; Soto-Valdez, H.; Matuana, L.; Rubino, M.; Auras, R. *Polym. Int.* 2012, *61*, 418.
- 8. Arrieta, M. P.; Lopez, J.; Ferrandiz, S.; Peltzer, M. A. Polym. Test. 2013, 32, 760.
- Al-Mulla, E. A. J.; Suhail, A. H.; Aowda, S. A. Ind. Crops Prod. 2010, 33, 23.
- Xiong, Z.; Yang, Y.; Feng, J.; Zhang, X.; Zhang, C.; Tang, Z.; Zhu, J. *Carbohydr. Polym.* **2012**, *92*, 810.

- 11. Al-Mulla, E. A. J.; Yunus, W.; Ibrahim, N. A. B.; Ab Rahman, M. Z. J. Mater. Sci. 2010, 45, 1942.
- 12. Silverajah, V. S. G.; Ibrahim, N. A.; Yunus, W.; Abu Hassan, H.; Woei, C. B. *Int. J. Mol. Sci.* **2012**, *13*, 5878.
- Silverajah, V. S. G.; Ibrahim, N. A.; Zainuddin, N.; Yunus, W.; Abu Hassan, H. *Molecules* **2012**, *17*, 11729.
- 14. Ali, F.; Chang, Y.-W.; Kang, S. C.; Yoon, J. Y. Polym. Bull. 2009, 62, 91.
- Baiardo, M.; Frisoni, G.; Scandola, M.; Rimelen, M.; Lips, D.; Ruffieux, K.; Wintermantel, E. J. Appl. Polym. Sci. 2003, 90, 1731.
- Ljungberg, N.; Andersson, T.; Wesslen, B. J. Appl. Polym. Sci. 2003, 88, 3239.
- Murariu, M.; Da Silva Ferreira, A.; Alexandre, M.; Dubois, P. Polym. Adv. Technol. 2008, 19, 636.
- Lemmouchi, Y.; Murariu, M.; Dos Santos, A. M.; Amass, A. J.; Schacht, E.; Dubois, P. *Eur. Polym. J.* 2009, 45, 2839.
- Wang, R. Y.; Wan, C. Y.; Wang, S. F.; Zhang, Y. Polym. Eng. Sci. 2009, 49, 2414.
- 20. Sierra, J.; Noriega, M.; Cardona, E.; Ospina, S. Presented at ANTEC 2010, Orlando, Florida, May 2010, p 127-132
- 21. Courgneau, C.; Domenek, S.; Guinault, A.; Averous, L.; Ducruet, V. J. Polym. Environ. 2011, 19, 362.
- 22. Labrecque, L. V.; Kumar, R. A.; Davé, V.; Gross, R. A.; McCarthy, S. P. J. Appl. Polym. Sci. 1997, 66, 1507.
- 23. Kulinski, Z.; Piorkowska, E.; Gadzinowska, K.; Stasiak, M. *Biomacromolecules* **2006**, *7*, 2128.
- 24. Kulinski, Z.; Piorkowska, E. Polymer 2005, 46, 10290.
- 25. Hu, Y.; Rogunova, M.; Topolkaraev, V.; Hiltner, A.; Baer, E. *Polymer* **2003**, *44*, 5701.
- Hu, Y.; Hu, Y. S.; Topolkaraev, V.; Hiltner, A.; Baer, E. Polymer 2003, 44, 5711.
- 27. Li, H.; Huneault, M. A. Polymer 2007, 48, 6855.
- Martino, V.; Ruseckaite, R.; Jiménez, A. J. Therm. Anal. Calorim. 2006, 86, 707.
- 29. Martino, V. P.; Jimenez, A.; Ruseckaite, R. A. J. Appl. Polym. Sci. 2009, 112, 2010.
- Hamann, C. P.; Plamthottam, S. S.; Smarthealth, I. WO Pat. WO201103479 A2 (2011).
- 31. Hamann, C. P.; Plamthottam, S. S.; Smarthealth, I. WO Pat. EP2584925 A2 (2011).
- 32. van Krevelen, D. W.; te Nijenhuis, K. Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions; Elsevier: Amsterdam, 2009; Chapter 7, p 189.
- Bondi, A. A. Physical Properties of Molecular Crystals, Liquids and Glasses; Wiley: New York, 1968.
- 34. Van Krevelen, D. W. Fuel 1965, 44, 229.
- 35. Van Krevelen, D. W.; Hoftyzer, P. J. J. Appl. Polym. Sci. 1967, 11, 2189.
- Abbott, S. J. Poly(lactic acid): Synthesis, Structures, Properties, Processing, and Applications; Wiley: Hoboken, NJ, 2010; Chapter 7, p 83.

- 37. Hyon, S. H.; Jamshidi, K.; Ikada, Y. Polym. Int. 1998, 46, 196.
- 38. Auras, R.; Harte, B.; Selke, S. Macromol. Biosci. 2004, 4, 835.
- Saeidlou, S.; Huneault, M. A.; Li, H.; Park, C. B. Prog. Polym. Sci. 2012, 37, 1657.
- 40. Pillin, I.; Montrelay, N.; Grohens, Y. Polymer 2006, 47, 4676.
- 41. Murariu, M.; Ferreira, A. D.; Alexandre, M.; Dubois, P. Polym. Adv. Technol. 2008, 19, 636.
- Stoclet, G.; Lefebvre, J. M.; Seguela, R.; Vanmansart, C. Polymer 2014, 55, 1817.
- 43. Moorshead, T. C.; Advances in Polymer Science; Sons, M. K. London, **1962**.
- Piorkowska, E.; Kulinski, Z.; Galeski, A.; Masirek, R. *Polymer* 2006, 47, 7178.
- 45. Ishikawa, M.; Ogawa, H.; Narisawa, I. J. Macromol. Sci. Phys. 1981, 19, 421.
- 46. Donald, A. M.; Kramer, E. J. Polymer 1982, 23, 1183.
- Donald, A. M.; Kramer, E. J. J. Polym. Sci. Polym. Phys. Ed. 1982, 20, 899.
- Dettenmaier, M.; Kausch, H. Advances in Polymer Science; Springer: Berlin, 1983; Vols. 52–53, p 57.

- 49. Kramer, E.; Berger, L. In Crazing in Polymers; Kausch, H. H., Ed.; Springer: Berlin, **1990**; Vol. 2, Chapter 1, p 1.
- 50. Wang, L.; Ma, W.; Gross, R. A.; McCarthy, S. P. Polym. Degrad. Stab. 1998, 59, 161.
- 51. Broz, M. E.; VanderHart, D. L.; Washburn, N. R. *Biomaterials* 2003, *24*, 4181.
- 52. Ma, X.; Yu, J.; Wang, N. J. Polym. Sci. Part B: Polym. Phys. 2006, 44, 94.
- 53. Jiang, L.; Wolcott, M. P.; Zhang, J. *Biomacromolecule* **2005**, 7, 199.
- 54. Shibata, M.; Inoue, Y.; Miyoshi, M. Polymer 2006, 47, 3557.
- 55. Odent, J.; Raquez, J. M.; Duquesne, E.; Dubois, P. Eur. Polym. J. 2012, 48, 331.
- NatureWorks. Technology Focus Report: Toughened PLA Ver. 3/1/2007. http://www.natureworksllc.com/~/media/Technical_ Resources/Technical_Publications/White_Papers/Toughened-PLA-Technology-Focus-pdf.pdf, accessed April 17, 2014.
- 57. Wypych, G. Handbook of Plasticizers; ChemTech: Toronto, 2004.