

Material Properties

Biopolymers: overview of several properties and consequences on their applications

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Abstract

Recently, interest in composite manufacturing has shifted towards the use of natural fibres as reinforcement because of their environmental benefits. The use of a biodegradable matrix is worth considering since this would result in a completely biodegradable composite.

In order to assess the most suitable matrix polymer, one must know the properties of the available polymers. Since data tend to be widely scattered over many sources and are very scarce compared to the conventional polymers, it is the purpose of this article to give an overview of the most relevant properties of a range of biodegradable polymers. An overview such as the one given here may provide a useful guide in establishing the best compromise between conflicting property demands. Data are presented mostly as ranges (in tables) as well as in graphs for quick comparison reasons. One specific application (thermoplastic pultrusion with flax as reinforcement) is also studied. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Before discussing the different properties of a series of biodegradable polymers [1–25], it may be interesting to elaborate on their current applications.

Many of these applications can be found in the medical field and can be roughly divided into three categories: drug delivery systems, wound closure and healing products, and surgical implant devices [9]. Drug delivery inside the human body can be quite easily controlled with the use of biodegradable capsules [9,31]. In wound healing, resorbable non-wovens for the replacement of human tissue [27], as well as simple sutures, staples, clips or meshes are available [9,28–30]. Related to these

applications, also the use as bioresorbable scaffolds for tissue engineering [22] is worth mentioning.

Other applications are numerous. Many of the biodegradable polymers have good film forming properties, making them suitable for applications in high performance applications as well as in traditional commodity uses [13]. Some applications include food containers, soil retention sheeting, agriculture film, waste bags [16] and the use as packaging material in general [31]. When used as non-wovens, these biopolymers can also be used in agriculture, filtration, hygiene and protective clothing [26].

This list of possible applications is by no means complete. In fact, the number of possible applications is almost infinite. It has also to be remarked that many of the applications involve the fibre form of the biopolymer. Since this paper considers the use as matrix material in a composite, fibre properties are not relevant. However, a few fibre properties will also be discussed.

The quantity of available data is rather limited compared to the data that can be found on conventional poly-

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mers. Therefore a restriction is made in the number of listed properties and studied polymers. More detailed but fragmented data can be found in the consulted literature [1–49]. Many of the data given here varied according to the source [1–25] consulted. Part of this variance is due to differences in standards used. However, most of the differences are thought to be due to differences in polymer types: degree of polymerisation, type and concentration of additives, etc. Besides the overall property ranges, individual data points are also given (in graphs) which gives a better understanding of the mean reported properties.

Composites are commonly based on traditional reinforcement fibres, such as glass fibres. However, natural fibres can also be used as reinforcement. One of the most cited natural fibres for this purpose is flax. This case will be more intensively studied in this paper, but in fact any other case study can be based on the reported properties.

2. Studied materials and properties

There are numerous biodegradable polymers. However, four basic polymers have been chosen, as well as two copolymers and two optically active polymer forms. This selection was based on the quantity of available data for all the reported biopolymers. For convenience reasons, from now on, these polymers will be denoted by their abbreviations:

PLA: Polylactic acid or polylactide.

L-PLA: Poly-L-lactic acid or poly-L-lactide.

DL-PLA: Poly-DL-lactic acid or poly-DL-lactide.

PGA: Polyglycolic acid or polyglycolide.

DL-PLA/PGA 50/50: copolymer of 50% DL-PLA and 50% PGA (molar percentages).

DL-PLA/PGA 75/25: copolymer of 75% DL-PLA and 25% PGA (molar percentages).

PCL: Poly- ϵ -caprolactone.

PHB: Polyhydroxybutyrate.

The structural formulas of the four basic polymers are given in Fig. 1. All these polymers are polyesters. Furthermore, PLA contains an asymmetrical carbon atom in its structural unit that enables it to become optically active. In this way, it is possible to obtain the isotactic L-PLA and D-PLA polymers. Consequently, DL-PLA is a syndiotactically alternating D,L-copolymer or a copolymer having L- and D-units. However, the exact nature of this D,L-copolymer is never explicitly stated in the literature. Mostly, even no D- or L-designation can be found. The latter findings have been gathered under 'PLA' and are thought to be mostly non-syndiotactic DL-PLA.

Both polylactide and polylactic acid (or polyglycolide

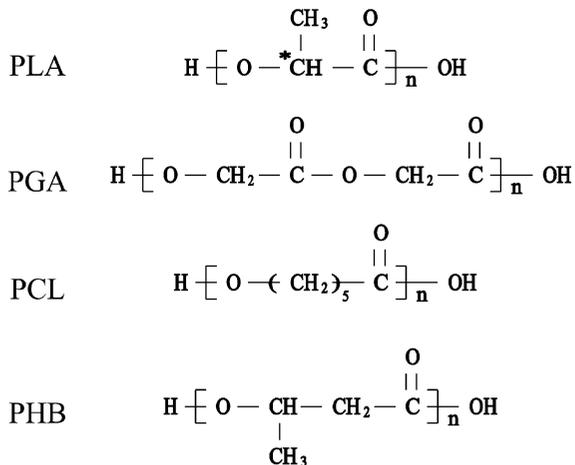


Fig. 1. Structural formulas of some biopolymers [19,25,26,32].

and polyglycolic acid) are terms that are used. PLA (and PGA) can be made from the original acid as well as from the cyclic lactide (or glycolide). These last products can be obtained by intermolecular splitting of water from the acids. The lactides are, furthermore, still optically active as can be seen in Fig. 2. Also visible in this figure is the fact that also a meso-lactide, which is optically not active, can be formed [3].

The following properties are more intensively studied:

- Polymer density (ρ , in g/cm^3).
- Tensile properties: tensile strength (σ , in MPa), tensile modulus (E , in GPa) and ultimate strain (ϵ , in %).
- Specific tensile properties are obtained by dividing the original properties by the polymer density, leading to: specific tensile strength (σ^* , in Nm/g) and specific tensile modulus (E^* , in kNm/g).
- Characteristic temperatures: glass transition temperature (T_g , in $^\circ\text{C}$) and melt point (T_m , in $^\circ\text{C}$).

Less documented cases on other properties and biopolymers could also be found in the literature. These data were too fragmentary to be included in the tables and graphs. However, attention will also be drawn to these properties if considered important enough.

Further details on these properties will be given later. Mostly, no reference to the used standard could be found. The standards quoted for the determination of certain properties are therefore not always the only possible ones used.

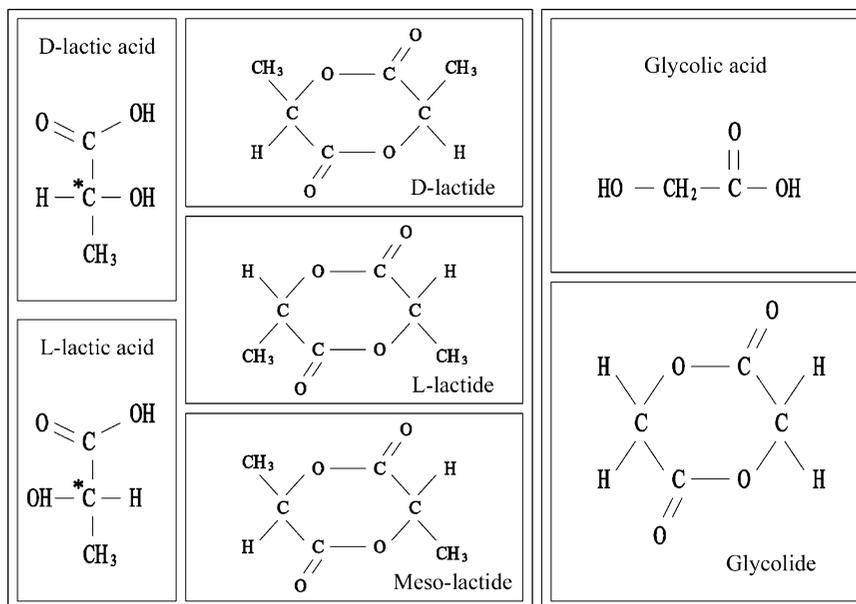


Fig. 2. Structural formulas of some monomers for the production of PLA and PGA [3,16].

3. Properties

3.1. Physical properties

The density of a series of biopolymers is given in Table 1 and Fig. 4. Reported values are mostly based on standards such as ASTM D792. Density can be a very important design parameter since elevated density values imply high transportation costs (e.g. light car parts reduce energy consumption). Implementation of the material also becomes much easier and less hazardous when lighter. Density is often used for the calculation of 'specific properties', i.e. dividing mechanical properties by the appropriate density. These specific properties consequently give a better notion of the intrinsic strength of the construction one wants to build. This will be explained later in Section 3.3.

In the case of flax reinforcement, (DL)-PLA, PCL and PHB seem to be the best choices since it is the purpose to produce a composite as light as possible. Apart from the values given in Table 1 and Fig. 4, the density data — 1.02 g/cm³ — found on PHO (polyhydroxyoctanoate) may also seem interesting [13]. However, calculation of the specific mechanical properties might result in different conclusions.

Aiming for a low density can also be a reason for selecting flax as composite reinforcement: its density of 1.45 g/cm³ is significantly lower than that of the more conventional glass fibre reinforcement (2.54 g/cm³).

Fragmented data on several other useful properties could be found: crimp [5,20], melt flow indices [1–

5,12,17,22,33,34,39,40], impact properties [2,3,5,12,17,32], hardness [12,14,17], vapour transmission characteristics (mainly for film applications) [1,4,13,18,35–37], compostabilities [1,2,33–37], coefficients of friction [1], surface energies [1] and contact angles with water [38]. Since data on these and other properties were so fragmentary, they were nearly impossible to evaluate.

A very important property is the water content or water uptake of the biopolymer resin. Only values for PLA resins are known [4,38] and they are situated near 0.5%. In fact the main PLA manufacturer (Cargill Dow) explicitly specifies that water should be removed from the resin — by drying — up to a level below 250 ppm, in order to make good processing of the pellets possible. All the biopolymers studied here are rather hydrophilic polyesters and so it is believed that moderate water uptake takes place when these polymers are exposed to water. Especially in composites, water absorption should be considered a disadvantage. Migration of water through the polymer can lead to a disturbance of the fibre/polymer interface, reducing the overall strength of the composite. In the case of flax reinforcement this could be even more dramatic since flax tends to absorb rather large amounts of water when exposed to it. The resulting swelling could lead to severe loss in composite strength. It might therefore be necessary to modify the flax in order to lower its water uptake significantly. The similarity between matrix and fibre polarities, on the other hand, might prove to enhance adhesion.

Compared to conventional polypropylene (PP) that

Table 1
Physical properties of various biopolymers [1–25]

Properties	Limits	Type of biopolymer							
		PLA	L-PLA	DL-PLA	PGA	DL-PLA/PGA 50/50	DL-PLA/PGA 75/25	PCL	PHB
ρ (g/cm ³)	Upper	1.21	1.24	1.25	1.50	1.30	1.3	1.11	1.18
	Lower	1.25	1.30	1.27	1.707	1.40		1.146	1.262
σ (MPa)	Upper	21	15.5	27.6	60	41.4	41.4	20.7	40
	Lower	60	150	50	99.7	55.2	55.2	42	
E (GPa)	Upper	0.35	2.7	1	6	1	1.38	0.21	3.5
	Lower	3.5	4.14	3.45	7	4.34	4.13	0.44	4
ϵ (%)	Upper	2.5	3	2	1.5	2	2.5	300	5
	Lower	6	10	10	20	10	10	1000	8
σ^* (Nm/g)	Upper	16.8	40.0	22.1	40.0	30.9	31.8	18.6	32.0
	Lower	48.0	66.8	39.4	>45.1	41.2	42.5	36.7	33.9
E^* (kNm/g)	Upper	0.28	2.23	0.80	4.00	0.77	1.06	0.19	2.80
	Lower	2.80	3.85	2.36	4.51	2.14	2.12	0.38	2.97
T_g (°C)	Upper	45	55	50	35	40	50	−60	5
	Lower	60	65	60	45	50	55	−65	15
T_m (°C)	Upper	150	170	am.	220	am.	am.	58	168
	Lower	162	200		233			65	182

am.: amorphous and thus no melt point.

was in a previous paper [50] selected as the most convenient conventional thermoplastic matrix, the densities found here are rather high.

Another important property is the degradation time [4,9,14,19]. With respect to disposal policy, this degradation time should be as short as possible. Corrosion resistance, on the other hand, might decrease too heavily when the polymer has an extremely short degradation time. Depending upon the source and the test procedure, these times range from several months (for the PLA/PGA copolymers) to over 2 years (for L-PLA). PGA and (DL)-PLA degrade after roughly 1 year. No data on PHB could be found. Based on these limited data, one can already conclude that the PGA/PLA copolymers seem to degrade too quickly to consider them for use in high performance composites.

3.2. Mechanical properties

Only tensile properties (ASTM D882, ASTM D638) are given in Table 1 and Fig. 3. These properties include: tensile strength (σ , in MPa), tensile modulus (E , in GPa), and ultimate tensile strain (ϵ , in %). No flexural properties are given here since data on these properties [3–5,18,41] was too limited to use in a comparison. Flexural and tensile properties are mostly correlated anyway and

the tendencies found here, are probably the same as found when comparing flexural properties.

Tensile properties are clearly best for the densest reported polymers, especially for PGA. PCL, on the other hand, seems to be the weakest polymer with a remarkable high strain at failure. It has to be remarked that molecular mass can play a very important role in the obtained mechanical properties. Varying the molecular mass from 50,000, over 150,000 to 200,000 will yield tensile strengths for L-PLA [3] of 15.5, 80 and 150 MPa, respectively.

When used as a matrix in a unidirectional composite, however, these mechanical polymer properties are not very important since the reinforcing (flax) fibre provides most of the composite strength [50]. For example, when a composite with a strength of 400 MPa and modulus of 23 GPa is required, one can calculate the volume percentage (v_f) that is needed, using a rule of mixtures. If a strength of 750 MPa and a modulus of 45 GPa is taken for the reinforcement (typical for flax), this results in the volume percentages given in Table 2. Typical polymer properties that are also needed for the calculation are also given in Table 2. Again using the rule of mixtures, the composite density can be obtained as well (Table 2; flax density is set at 1.45 g/cm³). Apparently the presence of PGA leads to the heaviest types of composites (with

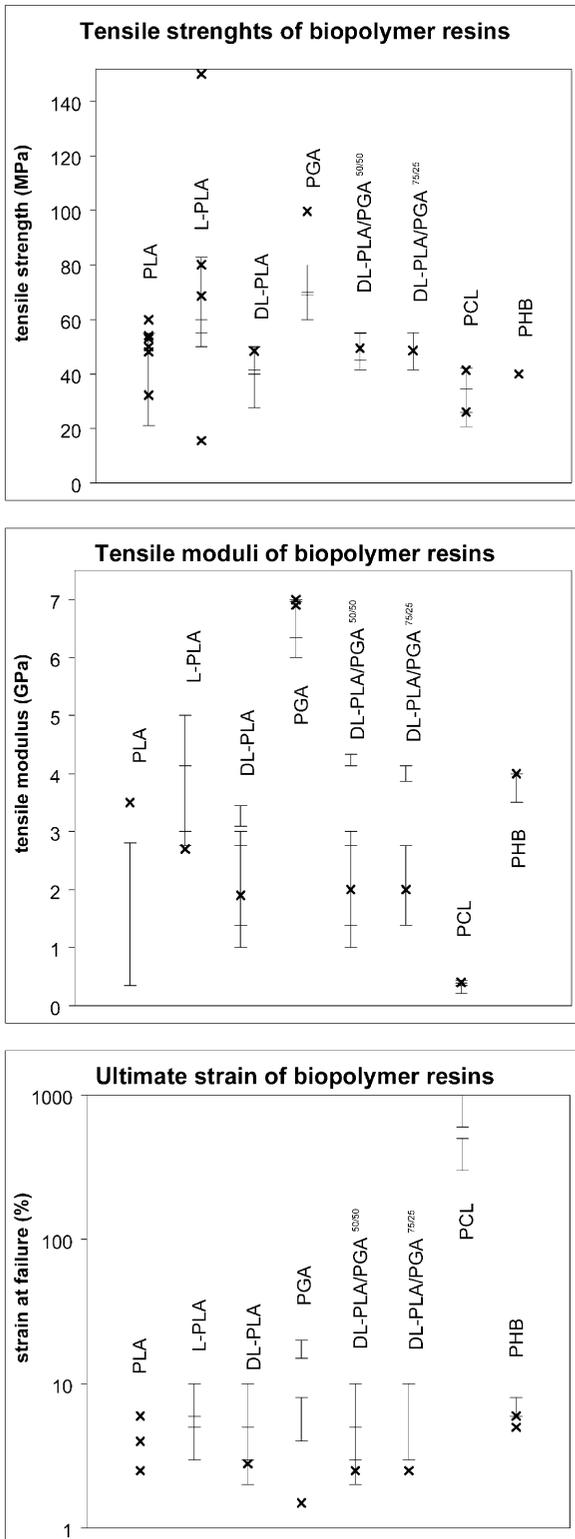


Fig. 3. Tensile properties of various biopolymers [2–5,7,9,12–19].

equal mechanical properties). PLA and PCL seem to lead to the lightest composites, with a relatively high v_f needed. High v_f values may be desirable since this would result in less use of expensive polymer (as far as good wetting of the fibre is still achievable). Even a biopolymer as weak as PHO (polyhydroxyoctanoate) with $\sigma=9$ MPa and $E=8$ MPa [13] would be suitable as a matrix, since the v_f needed is hardly any higher (51–53%) than the ones given in Table 2. The resulting composite density would be even lower (1.24–1.25 g/cm³) than the one for PCL/flax. It seems that the weaker the matrix polymer gets, the lighter the resulting composite will be, while the composite mechanical properties seem hardly affected at all.

In order to have a broader view on the effect of matrix type on the expected composite properties, one can also look at Figs. 6 and 7. These figures show the expected composite properties — expressed as specific properties — as a function of the reinforcement level. By using specific properties, the difference in density is also taken into account. Again PLA and PCL (also PHB) seem to be the best candidates for composite matrix use. This is most clear in the detailed parts of the figures, which are chosen to be the most likely v_f interval. It is also clear that increasing use of PGA progressively leads to composites with worse specific mechanical properties.

Up till now — based on the densities and mechanical properties — preference for the selected application (pultrusion with flax as reinforcement) is given to PLA and PCL, or any light biopolymers in general.

3.3. Specific mechanical properties

In Fig. 4 one can find the specific tensile strength and tensile modulus ranges for the different biopolymers. These values were obtained by dividing the original mechanical properties by the density. If either density or the mechanical property was not available within the same reference, no specific data were calculated. This restriction was necessary since it is likely that the polymers' density is related to its mechanical properties.

If one would like to use the biopolymers as structural element without using reinforcement, specific properties become important as they determine the dimensions necessary for a certain mechanical strength or stiffness.

Contrary to the usefulness as composite matrix, in this case, PGA and L-PLA seem the best choices, whilst PCL and also PHO (polyhydroxyoctanoate, $\sigma^*=8.8$ MPa and $E^*=7.8$ MPa) are clearly the worst ones.

3.4. Characteristic temperatures

Characteristic temperatures of a polymer can be determined in several ways, but DSC (differential scanning calorimetry) is the most cited one.

The flexibility of amorphous polymers is reduced

Table 2

Composition and density of flax fibre based composites with $\sigma=400$ MPa and $E=23$ GPa

Biopolymer type	Typical polymer properties			Composite ($\sigma=400$ MPa and $E=23$ GPa) properties			
	σ (MPa)	E (GPa)	ρ (g/cm ³)	Based on desired σ		Based on desired modulus	
				v_f (%)	ρ (g/cm ³)	v_f (%)	ρ (g/cm ³)
PLA	50	2.5	1.24	50.0	1.35	48.2	1.34
L-PLA	75	3.0	1.26	48.1	1.35	47.6	1.35
DL-PLA	45	2.5	1.26	50.4	1.36	48.2	1.35
PGA	75	6.5	1.61	48.1	1.53	42.9	1.54
DL-PLA/PGA 50/50	50	2.5	1.35	50.0	1.40	48.2	1.40
DL-PLA/PGA 75/25	50	2.5	1.30	50.0	1.38	48.2	1.37
PCL	30	0.35	1.13	51.4	1.29	50.7	1.29
PHB	40	4.0	1.24	50.7	1.35	46.3	1.34

Typical flax properties: $\sigma=750$ MPa and $E=45$ GPa.

drastically when they are cooled below a characteristic transition temperature called the glass transition temperature (T_g). At temperatures below T_g , there is no segmental motion and any dimensional changes in the polymer are the result of temporary distortions of the primary valence bonds. Amorphous plastics — such as all the DL-PLA containing ones — perform best below T_g , but elastomers must be used above the brittle point [42]. The glass transition temperature (given in Table 1 and Fig. 5) can be very important when studying mechanical properties. These properties are always obtained in standard conditions (comparable to room temperature), but one should know that they may decrease at higher temperatures and that the glass transition temperature may be a limit above which mechanical properties may degrade drastically.

In the specific case of a flax reinforced plastic, the application temperature of the product should remain relatively low (e.g. maximum 100°C) because of the possible degradation of flax when exposed to elevated temperatures for prolonged time (Figs. 6 and 7). All the studied biopolymers have already surpassed their T_g at this temperature but this is not necessarily a problem since the major part of the composite strength (unidirectionally reinforced composite) is determined by its fibres. However, all DL-PLA containing biopolymers can probably be rejected for use in composites since — besides their low T_g (40–60°C) — they are amorphous. PGA and PHB have a T_g near to regular ambient temperatures. Further study of the mechanical properties above these temperatures should be done prior to using these polymers as composite matrix in applications above regular ambient temperatures. The same can be said about PHV (polyhydroxyvalerate) with a T_g of 5°C [43] and Biopol (PHB/PHV copolymer with 5–12% PHV) with a T_g of 18–22°C [32]. The other studied

biopolymers (PCL, L-PLA and PLA) would probably do better since their glass transition temperatures are distinctly different from normal ambient temperatures. On this basis also PHO (polyhydroxyoctanoate) would be acceptable for use as matrix material since its T_g is -35°C [13].

The melting point (T_m , also given in Table 1 and Fig. 5) is a more important parameter. Above it, whole polymer chain mobility occurs and the mechanical properties are virtually reduced to zero. Together with the melt points one should also look at the process temperatures. These are by definition significantly higher than the melt points because at these higher temperatures viscosity is reduced drastically in order to improve processability. These temperatures are not given in Table 1 since only data on PLA, ranging from 190 to 250°C [1,2,5,20,33–37], could be found. Generally the processing temperatures are 20–100°C higher than the melt points [50]. This range mainly depends upon the use of additives that can prevent thermal degradation of the polymer at elevated temperatures. A low process temperature (and melt point), on the other hand, may be advantageous when considering the energy cost of the production process.

In the specific studied case, temperatures already have to be kept relatively low in order to prevent the degradation of the flax. And since the purpose is to produce an environmentally friendly product, low energy consumption is to be considered as an extra advantage. Studying Fig. 5 leads to the conclusion that PGA and PCL are not suited for use in combination with flax. PGA would require process temperatures — possibly higher than 250°C — that would lead to thermal degradation of the flax, while PCL has such a low melt point that application of the composite should be limited to temperatures below 58°C. This is also the case for PHO (polyhydroxyoctanoate) with a melt point of 61°C [13]

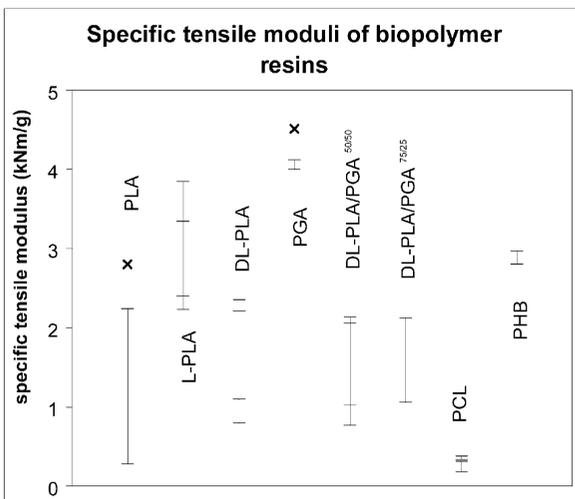
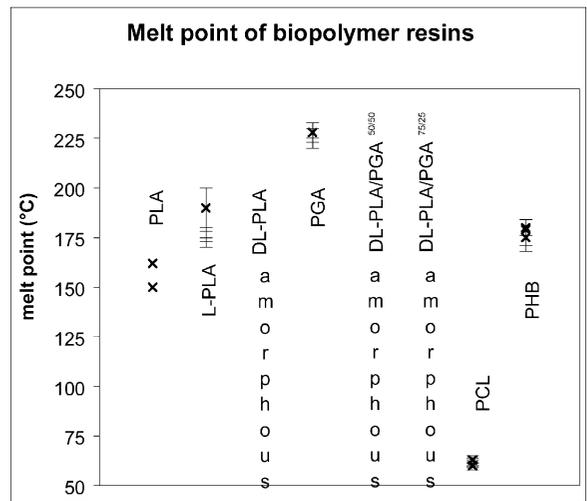
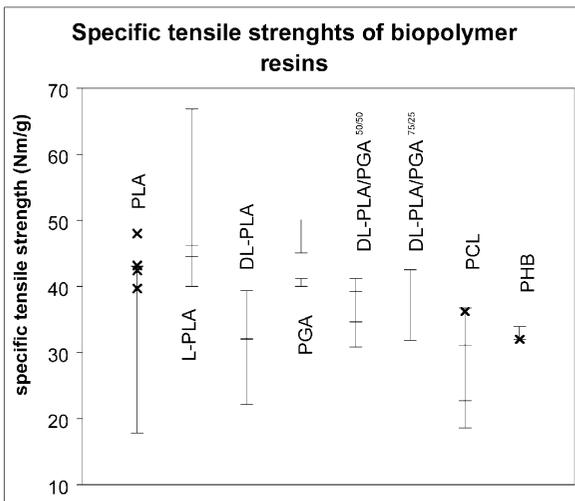
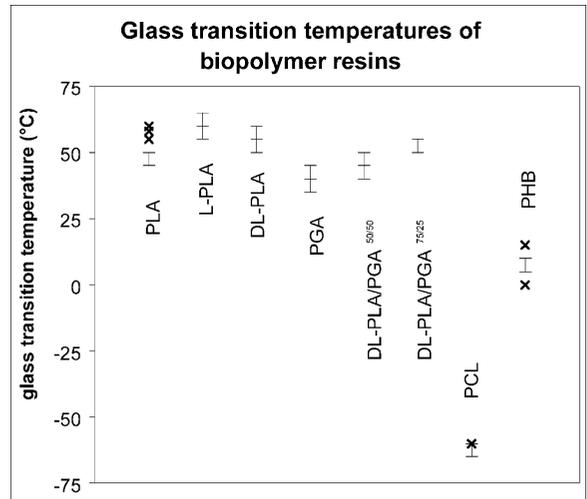
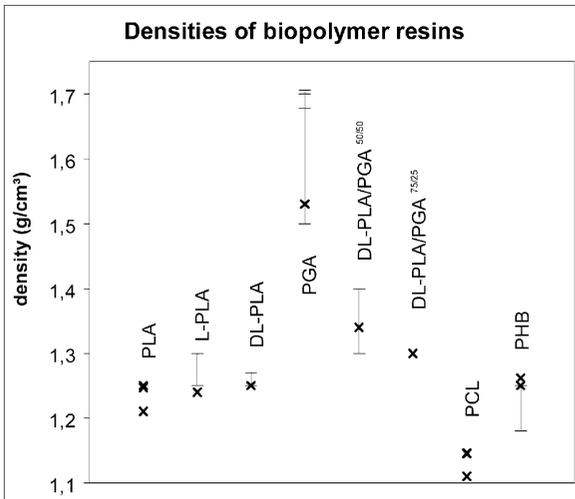


Fig. 5. Thermal properties of various biopolymers [1,3,4,6,8–13,15–25].

Fig. 4. Densities and specific tensile properties of various biopolymers [1–13,15].

and, to a lesser extent, for PHV (polyhydroxyvalerate) with a melt point of 105–108°C [3]. L-PLA, PLA and PHB have all ideal melt points since they are high enough for sufficient thermal stability of the composite as well as low enough to limit flax degradation and energy costs. The same can be said for Biopol (PHB/PHV copolymer with 5–12% PHV) with a melt range from 144 to 170°C [3,32].

Only crystalline polymers have a melting point. Furthermore, crystalline regions in the polymer tend to improve the adhesion with a reinforcing fibre. Percentages of crystallinity found in literature range from 25% for PHO to 80% for PHB [3,13,18,19,44]. All other listed crystalline polymers have comparable percentages of crystallinity (37–55%). Based on crystallinity, preference for use in composites should be given to PHB.

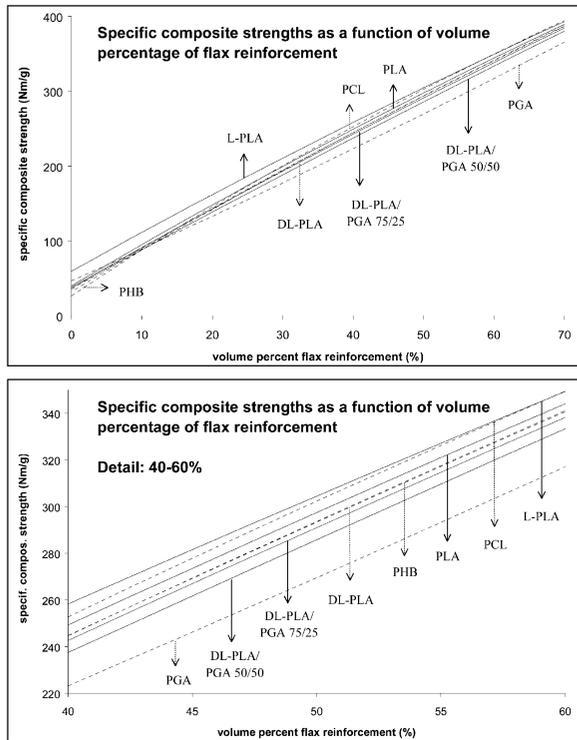


Fig. 6. Specific composite strengths as a function of volume percentage of flax reinforcement.

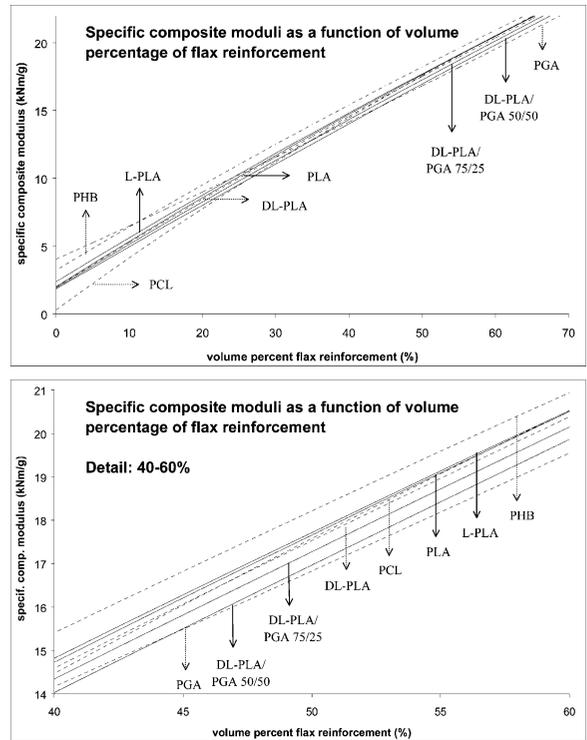


Fig. 7. Specific composite moduli as a function of volume percentage of flax reinforcement.

3.5. Fibre mechanical properties

Sometimes, mechanical properties of polymer fibres can be found. As an example, tenacity (tensile strength, in MPa) and tensile modulus (in GPa), together with the production methods of some biopolymers are given in Table 3. It should be clear that these values cannot be used for design calculations unless the fibres are kept in their original form. The fibres display such high mechanical properties because of the high degree of orientation of the polymer chains in the fibre. The influence of the polymer type apparently is of secondary importance and only becomes important when the material is melted again.

4. Conclusions

It has been the purpose of this paper to search for the most suitable thermoplastic biopolymer matrix for a flax fibre reinforced composite. Density and temperature related properties seemed to be the limiting criteria for the choice of a suitable polymer. As has been pointed out, the mechanical strength of the biopolymer is not very important for this particular application.

PGA is easily eliminated as a candidate for composite

Table 3
Biopolymer fibre properties [28–30,33,34,45–49]

Biopolymer type	Fibre production method	σ (MPa)	E (GPa)
PLA	conventional melt spinning	313–642	5.6
L-PLA	melt spinning + hot drawing	500–870	9.2
L-PLA	solvent spinning + hot drawing	1000–1200	12–15
DL-PLA	dry spinning or melt spinning + hot drawing	190–1000	(data not available)
PHB	high-speed melt spinning + hot drawing	330	7.7

matrix use as its density and melt point are too high in order to be energy saving. Also, high processing temperatures would cause flax degradation. PCL on the other hand may be light enough but its melt temperature is too low in order to be used in a composite exposed to slightly elevated temperatures. The DL-PLA/PGA copolymers seem to be too easily degraded, which could be an indication of low corrosion resistance, and furthermore they are amorphous which would lead to bad adhesion with the reinforcing fibre. In fact, any studied polymer based on DL-PLA is amorphous and glass transition temperatures are too low to ensure resistance to slightly elevated temperatures. Some other, not well-documented biopolymers can also be eliminated for use as matrix in flax fibre reinforced composites. For instance PHO may lead to light composites but its melt temperature is too low (as is the case for PHV).

PLA (and L-PLA) seem to score well on all the discussed properties: polymer and composite densities are low; degradation behaviour, mechanical properties and glass transition temperatures are acceptable and their melt points are almost ideal in order to produce flax fibre reinforced composites. Preference should be given to PLA rather than to L-PLA since the latter is likely to be more expensive and PLA is already commercially available.

The use of PHB or PHB based copolymers such as Biopol may also be possible in this studied case. Density and melt point are optimal for these polymers but the low glass transition temperature may be a problem.

Since all studied biopolymers are likely to be sensitive to water, it is probably also necessary to modify the flax in order to render it less sensitive to water.

In general, the properties that are reported here may help to decide on choosing the right biopolymer for many given problems. As already mentioned, one best first selects some limiting properties and then further selects the polymer with the best overall properties.

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References

- [1] PLA Polymer 1100D — A Product from Nature Works®, Extrusion Coating Product Information, Cargill Dow LLC, pp. 1–2.
- [2] PLA Polymer 2000D — A Product from Nature Works®, Extrusion/Thermoforming Product Information, Cargill Dow LLC, pp. 1–2.
- [3] H.G. Fritz, T. Seidenstücker, U. Bölz, M. Juza, J. Schroeter, H.J. Endres, Use of whole cells and enzymes for the production of polyesters (chapter 3) and mimicking of natural substances (petroleum derived polymers) (chapter 4), in: Study on Production of Thermoplastics and Fibres Based Mainly on Biological Materials, European Commission — Science Research Development — Agro-Industrial Research Division, 1994, pp. 109–190.
- [4] Transparent and Flexible Biodegradable Plastics (CPLA), <http://www.dic.co.jp/green/index-e.html>, 1999, pp. 1–7.
- [5] PLA Polymer — A Product from Nature Works®, Injection Molding Process Guide, Cargill Dow LLC, pp. 1–2.
- [6] J. Brandrup, E.H. Immergut (Eds.), Polymer Handbook, 2nd ed., Wiley-Interscience, New York, 1975.
- [7] Physical Properties of Selected Polymers, Lactel Biodegradable Polymers (Birmingham Polymers Inc.), Technical Info via <http://www.birminghampolymers.com>.
- [8] BPI Material Safety Data Sheet, MSDS #: BPI-002, via <http://www.birminghampolymers.com>, p. 1.
- [9] Purasorb® Monomers and Biodegradable Polymers brochure obtained from PURAC Biochem NV, The Netherlands.
- [10] BPI Material Safety Data Sheet, MSDS #: BPI-001, via <http://www.birminghampolymers.com>, p. 1.
- [11] Polycaprolactone, Product number 440752, Sigma-Aldrich Technical Library, via <http://www.sigma-aldrich.com>
- [12] Polycaprolactone, Product number 440744, Sigma-Aldrich Technical Library, via <http://www.sigma-aldrich.com>
- [13] Polymer Properties, Metabolix Technology Profile, via <http://www.metabolix.com>
- [14] G.D. Biby, Degradable Polymers, via <http://www.icma.com>
- [15] S. Jacobsen, H.G. Fritz, Plasticizing polylactide — the effect of different plasticizers on the mechanical properties, Polymer Engineering and Science 39 (7) (1999) 1303–1310.
- [16] Biolac, via <http://members.rediff.com>
- [17] Polycaprolactone, Product number 181609, Sigma-Aldrich Technical Library, via <http://www.sigma-aldrich.com>
- [18] Biopol, via <http://members.rediff.com>
- [19] J.C. Middleton, A.J. Tipton, Synthetic Biodegradable Polymers as Medical Devices, via <http://www.devicelink.com>
- [20] K. Cink, Technical Guide for Using PLA in 2 stage ISBM Containers, Cargill Dow, 11-22-00.
- [21] Chemical Properties of Selected Polymers, Lactel Biodegradable Polymers (Birmingham Polymers Inc.), Technical Info via <http://www.birminghampolymers.com>
- [22] I. Zein, D.W. Hutmacher, S.H. Teoh, K.F. Tan, K.C. Tan, The Processing of Bioresorbable Scaffolds for Tissue Engineering Applications via Fused Deposition Modeling, via <http://eicu.tp.edu.sg>
- [23] Polycaprolactone, Product number 81277, Sigma-Aldrich Technical Library, via <http://www.sigma-aldrich.com>
- [24] Polycaprolactone, Product number 81277, Sigma-Aldrich Technical Library Specifications, via <http://www.sigma-aldrich.com>
- [25] Synthesis of biodegradable polymers, in: W. Schnabel (Ed.), Polymer Degradation, Hauser International, Wien, 1981, p. 169–173.
- [26] P. Ehret, Biodegradable nonwovens, ITB Nonwovens — Industrial Textiles, no. 3, 1996, pp. 29–30.
- [27] D. Eagles, D. Lesnoy, S. Barlow, Des tissues humains

- recr es   la demande, TUT, 1er Semestre, no. 23, 1997, pp. 41–42.
- [28] J.P. Penning, H. Dijkstra, A.J. Pennings, Preparation and properties of absorbable fibres from L-lactide copolymers, *Polymer* 34 (5) (1993) 942–951.
- [29] S. Gogolewski, A.J. Pennings, Resorbable materials of poly(L-lactide). II. Fibres spun from solutions of poly(L-lactide) in good solvents, *Journal of Applied Polymer Science* 28 (3) (1983) 1045–1061.
- [30] B. Eling, S. Gogolewski, A.J. Pennings, Biodegradable materials of poly(L-lactid Acid). I. Melt spun and solution spun fibres, *Polymer* 23 (11) (1982) 1587–1593.
- [31] Possible Applications of Selected Polymers, via <http://members.rediff.com>.
- [32] T. Hammond, J.J. Liggat, Properties and applications of bacterially derived polyhydroxylalkanoates, in: G. Scott, D. Gilead (Eds.), *Biodegradable Polymers*, Chapman and Hall, London, 1995, pp. 88–111.
- [33] PLA Polymer 6200D — A Product from Nature Works®, Continuous Filament and Staple Fibers, Cargill Dow LLC, pp. 1–2.
- [34] PLA Polymer 6700D — A Product from Nature Works®, High Strength Monofilament, Cargill Dow LLC, pp. 1–2.
- [35] PLA Polymer 4041D — A Product from Nature Works®, Biaxially Oriented Films — General Purpose, Cargill Dow LLC, pp. 1–2.
- [36] PLA Polymer 4040D — A Product from Nature Works®, Biaxially Oriented Films — General Purpose, Cargill Dow LLC, pp. 1–2.
- [37] PLA Polymer 4031D — A Product from Nature Works®, Biaxially Oriented Films — High Heat, Cargill Dow LLC, pp. 1–2.
- [38] Fiber Properties Comparison, January 11, 2000, Cargill Dow, p. 1.
- [39] Polycaprolactone, Product number 440744, Sigma-Aldrich Technical Library Specifications, via <http://www.sigmaaldrich.com>
- [40] Polycaprolactone, Product number 181609, Sigma-Aldrich Technical Library Specifications, via <http://www.sigmaaldrich.com>
- [41] D. Hutmacher, A. Kirsch, K.L. Ackermann, M.B. H rzeler, Development of a bioresorbable membrane fixation system, *Zeitschr. f. Zahn rtzl. Implantologie* 3 (1996).
- [42] N.B. Seymour, CH.E. Carraher, *Polymer Chemistry*, 5th ed., Marcel Dekker, Basel, 2000.
- [43] Physical Properties important for Processing of Bioplastics, via <http://members.rediff.com>
- [44] L. Fambri, A. Pegoretti, R. Fenner, S.D. Incardina, C. Migliaresi, Biodegradable fibres of poly (L-lactid acid) produced by melt spinning, *Polymer* 38 (1) (1997) 79–85.
- [45] Fibers Attributes, Cargill Dow, via <http://www.cdply.com>
- [46] J.S. Dugan, Novel properties of PLA fibers, via <http://www.fitfibers.com>
- [47] Y. Ikada, S. Gen, Poly(lactic acid) fibre, Daicel Industries Ltd., USP 5 010 145, 21 April 1987.
- [48] J.P. Penning, H. Dijkstra, A.J. Pennings, Preparation and properties of absorbable fibres from L-lactide copolymers, *Polymer* 34 (5) (1993) 942–951.
- [49] G. Schmack, D. Jehnichen, R. Vogel, B. Tandler, Biodegradable fibers of poly(3-hydroxybutyrate) produced by high-speed melt spinning and spin drawing, *Journal of Polymer Science* 38 (21) (2000) 2841–2850.
- [50] K. Van de Velde, P. Kiekens, Thermoplastic polymers: overview of several properties and their consequences in polymer/flax composites, *Polymer Testing* 20 (8) (2001) 885–893.