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GIUSEPPE SACCULLO

Advanced Ecocomposites Materials

PhD THESIS

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Introduction and Motivation

In the last decades, emerging terms such as ‘sustainable or green development’ raised an increasing interest from society and industry. The increasing awareness of the environmental issues concerning resources depletion and pollution pushed governments to release new rules about materials usage and processing methods. Environmental impact indicators like CO_2 consumption, Embodied Energy are becoming a common way to measure the performance of new materials and process in addition to mechanical and cost properties. Due to long term resistance of plastic materials their disposal is one of challenge nowadays. The use of biodegradable plastics instead of petroleum-based plastics is one of the most promising solutions to the environmental problems caused by the disposal of plastic wastes. The use of plastics from renewable sources is another way to approach the problem of the environmental impact of plastics. Combining biodegradable and renewable-based plastics is one of the optimum solutions to fulfil the goal of fully green mateirals. Commercial resin manufacturers started to invest seriously on the ECO brand by proposing several resin which, somehow, have some bio-based or recycled content. Fig.1 presents some exampls of brands of commercial resin manufacturers focusing all their business on the eco brand.

Figure 1- Commercially available eco-resins

However, the use of unreinforced plastics limits the applications of plastic itself. Traditional composites for semi-structural and structural applications requires the addition of mineral fillers in the form of particles or fibres. Glass and carbon fibers being the most used alternative. Life cycle assessment studies outlined that mineral based fillers negatively impact on the environment because of complex extraction and processing procedure to obtain them in usable form. This limitation moved the attention towards natural fiber-reinforced polymer composites.

The main advantages of using natural fibers as reinforcing fibers are:renewability, cheapness, recyclability, and biodegradability. Also their lower density and price together with satisfactory mechanical properties, compared to glass fibers, make them an attractive ecological alternative to glass fibers traditionally used for the manufacturing of fiber reinforced composites. In some cases, the unique damping properties of natural reinforced composites make them interesting for the production of hybrid carbon/natural fiber composites.

Natural fiber-containing composites are used in different applications, such as structural materials, building and construction industries, packaging, biomedical devices (Fig.2). Automotive is one of the most promising and expanding fields for the wide application of natural fiber composites in mass-volume productions (Fig.2).

Figure 2 - Natural Fiber composites application examples

Most of the applications of natural fiber composites still rely on traditional matrices. The use of renewable and biodegradable matrices is compulsory to ensure truly ecocomposites to be exploited.

Polylactic acid (PLA) is a polymer synthesizable from 100% renewable resources such as fermentation products of corn and sugar beets. Compared with other biopolymers, PLA is easy to be processed, and once formed it presents mechanical properties that are competitive with polypropylene and other engineering polymers. Many studies in the literature have investigated the use of PLA as a basis to obtain truly eco-composites.

Recently, a spin off company of Fraunhofer Institute named Tecnaro started the commercialization of a polymer branded as Arboform the “liquid wood” as a 100% polymer derived from lignin. Such a polymer has been presented as the solution to obtain truly 100% ecocomposites. Another relevant example in the field of eco-composites is represented by the parent companies Entropy Resins and Connora Technologies. The company Entropy produces a resin name SuperSap which is derived by pine oil and paper byproducts. The supersap resin is an epoxy based resin with a biocarbon content of about 45% which can be used in the automotive, naval and sportive goods sectors. Connora Technologies patented innovative ammine curing agents which are named cleavable as they contain a cleavable moiety which allow to recycle the cured thermoset into a reusable thermoplastic using mild acid treatments. By the combined use of

Entropy epoxy resins and Connora ammine a novel biobased and fully recyclable epoxy composites can be produced.

The aim of the present PhD was to develop novel formulations based on the use of renewable and biobased polymers to obtain truly ecocomposites reinforced with natural fibers and fillers. The research work focused both on thermoplastic and thermoset resins to achieve the development of biobased and recyclable resin systems suitable for both injection moulding and infusion based processing techniques.

The experimental research work on the thermoplastic matrices started by the study of the chemical structure of the polymer commercialized by Tecnaro under the name Arboform LV 100. This is a polymer claimed to be derived entirely from lignin and proposed for the use in injection molding. Following the characterization and reverse engineering of LV 100 the research work was based on the development of a novel formulation based on mixing PLA and lignin from commercial sources as base materials. To obtain a full range of properties PP was also considered as polymeric matrices for the development of biobased blends. All the blends were prepared by melt mixing and then processed by injection molding and, in some cases, Fused Deposition Modelling was also attempted. The blends were produced with different content of lignin.

A special focus of the research was on the understanding of thermal statbility of the blends during processing. The effect of melt mixing and of reprocessing on the mechanical and chemical properties of the blends studied was studied in the present thesis to unveil the recyclability of the developed blends.

The experimental research work on the thermoset matrices was mainly focused on the mixing of the Entropy resins with the Connora ammine. The blends mixed therefore were processed by the use of High Pressure Resin Transer Moulding (HP-RTM). HP-RTM is a novel technology which allow to prepare composite parts with processing cycle down to less than 10 minutes. This technology is currently used by BMW for the production of some parts of the i3 and i8 car models. The study on the biobased thermosets was carried out focusing on the mixing of the monomers, their processing in an industrial HP-RTM Cell and on the characterization of the composites prepared therefore and on their recycling. To increase the biobased content of the composites ensuring the preparation of green eco-composites natural fiber reinforcements were used. In order to guarantee high mechanical properties hybrid carbon/flax fabric layup were used.

The thesis is divided into five chapters: the first four chapters cover the state of the art review on wood plastic composites, lignin and the recycling of bioplastics. The fifth chapter cover the experimental work of the thesis. In chapter fifth the materials and methods used are firstly presented followed by the discussion on the results obtained.

Chapter 1 Natural fiber composites

1.1 Introduction

In the latest years industry is attempting to decrease the dependence on petroleum based fuels and products due to the increased environmental consciousness. This is leading to the need to investigate environmentally friendly, sustainable materials to replace existing ones. The tremendous increase of production and use of plastics in every sector of our life lead to huge plastic wastes. Disposal problems, as well as strong regulations and criteria for cleaner and safer environment, have directed great part of the scientific research toward eco-composite materials. Among the different types of eco-composites those which contain natural fibers (NF) and natural polymers have a key role. Since few years polymeric biodegradable matrices have appeared as commercial products, however their high price represents the main restriction to wide usage. Currently the most viable way toward eco-friendly composites is the use of natural fibres as reinforcement. Natural fibres represent a traditional class of renewable materials which, nowadays, are experiencing a great revival. In the latest years there have been many researches developed in the field of natural fibre reinforced plastics (Bledzki & Gassan,1999). Most of them are based on the study of the mechanical properties of composites reinforced with short fibers. The components obtained therefore are mostly used to produce non-structural parts for the automotive industry such as covers, car doors panels and car roofs (Magurno, 1999, John at als., 2008) (Fig.1,2).

Fig. 1. Mercedes-Benz A natural fibre composites components (source: DaimlerChrysler AG)

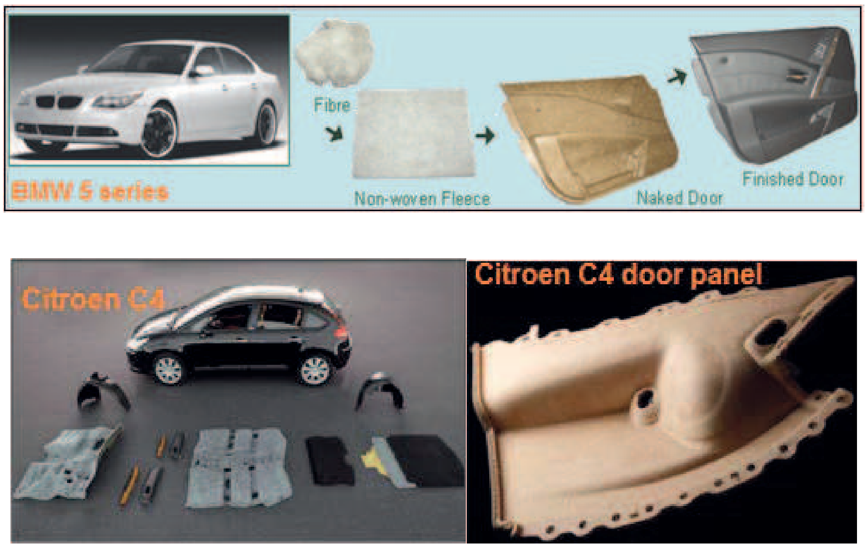


Fig. 2. Examples of applications of Natural Fibres in the automotive field

Few studies deal with structural composites based on natural reinforcements. These studies are mainly oriented to the housing applications where structural panels and sandwich beams are manufactured out of natural fibres and used as roofs (Saheb & Jog., 1999). Considering the high performance standard of composite materials in terms of durability, maintenance and cost effectiveness, the application of natural fiber reinforced composites as construction material holds enormous potential and is critical for achieving sustainability. Due to their low density and their cellular structure, natural fiber posses very good acoustic and thermal insulation properties and demonstrate many advantageous properties over glass or rockwool fibre (e.g. handling and disposal).

Nowadays natural fibre composites are not exploited only in structural and semi-structural applications of the automotive sector, but in other fields too (Fig.3).

Fig. 3. Examples of applications of Natural Fibres in several applications

Natural fibres (Fig.4) can be divided according to their origin: animal, vegetable and mineral. The most used are the vegetable ones due to their wide availability and renewability in short time respect to others, so when we say “natural fibres” we means vegetable ones. In the past, natural fibres were not taken into account as reinforcements for polymeric materials because of some problems associated with their use:

- Low thermal stability, in other terms the possibility of degradation at moderate temperature (230-250 ° C).
- Hydrophilic nature of fibre surface, due to the presence of pendant hydroxyl and polar groups in various constituents, which lead to poor adhesion between fibres and hydrophobic matrix polymers (John et als., 2008, Kalia et als., 2009). The hydrophilic nature can lead to

swelling and maceration of the fibers. Furthermore, moisture content decreases significantly fibre's mechanical properties.

- Properties variability depending on the quality of the harvest, age and body of the plant from which they are extracted, the extraction techniques and the environmental conditions of the site.

Lack of good interfacial adhesion, low melting point, and poor resistance towards moisture make the use of natural fibre reinforced composites less attractive than synthetic fibre (glass, carbon, aramid, etc.) that have been up to now the only choice for reinforcing polymeric composites, due to their superior mechanical properties. However, the production of composites reinforced with synthetic fibres and matrices requires a large amount of energy which is only partially recovered with incineration of fibre reinforced composites. This has once again drawn the attention towards natural fibres due to their environmental advantages. It has been demonstrated that the energy needed for production of natural fibres is, on average, more than half of the amount needed for synthetic fibres (Fig.5). Thus, the renewed interest in the natural fibers, due to their lightweight, nonabrasive, non irritating, combustible, nontoxic, biodegradable properties (Saheb & Jog, 1999), low energy consumption for production, budget zero CO_2 emissions if burned, low cost (Table 1), main availability and renewability compared to synthetic fibres, has resulted in a large number of applications to bring it at par and even superior to synthetic fibers. Because of such properties natural fibers are fast emerging as a viable choice as reinforcing material in composites (kalia et als., 2009).

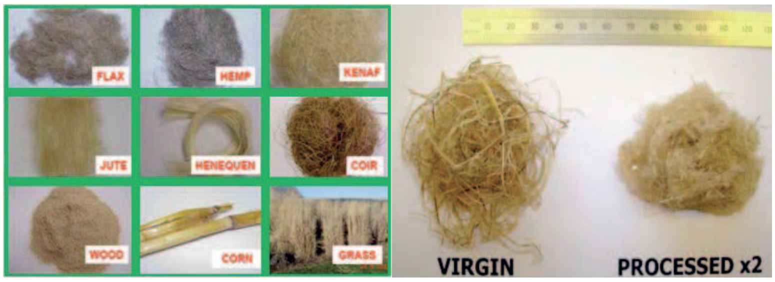


Fig. 4. (a) Some natural fibre, (b) Processed hemp fibre (source: University of Exeter)

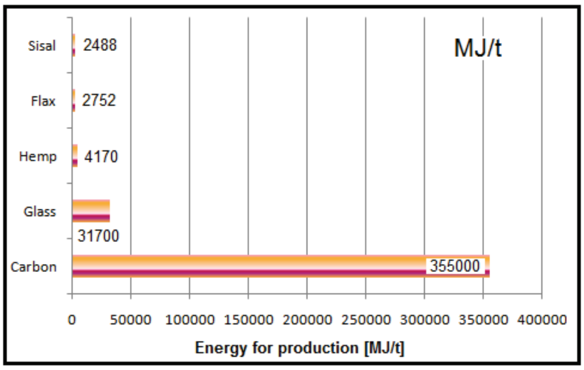


Fig. 5. Energy for production of some fibre

(sources: SachsenLeinen; Daimler 1999; BAFA; NOVA; AVB; CELC; REO)

Fiber	**Price**	**Specific Gravity**	**Price**
	$ /m^3	Kg/m^3	$ /kg
Wood	420	1600	0,26
Flax	600	1500	0,40
Glass	4850	2600	1,87
PP	650	900	0,72

Table 1. Cost comparison between natural and synthetic fibre *(Source: Georgia Institute of Technology www.me.gatech.edu/jonathan.colton/me4793/natfiber.pdf)*

Even if natural fibre has a very low energy consumption for production compared to other synthetic fibre, such as glass or carbon, careful environmental impact evaluation must be take in consideration in order to make the right choice. In fact, the validity of “green” case for substitution of synthetic fibre by natural ones is dependent on the type of reinforcement and related production processes. A parameter which better describe the environmental impact is the *embodied energy* calculated with reference to all related agricultural operations (from ploughing to harvest), fibre extraction operations (retting and decortication), fibre preparation operations (hackling and carding), fibre processing operations (spinning or finishing) and materials used for these operations. The use of Embodied energy reveals that not any kind of natural fibre reinforcement is “greener” then synthetic ones. Fig. 6 shows that, even if adopting the most environmental friendly option (no-till and water retting) for flax fibre production, only mat fabrics are, in energetic terms, “greener” while flax yarns has a higher embodied energy respect to glass fibre continuous filament production.

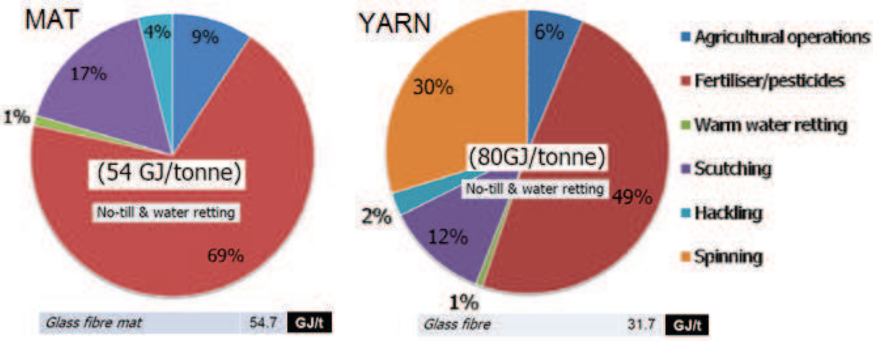
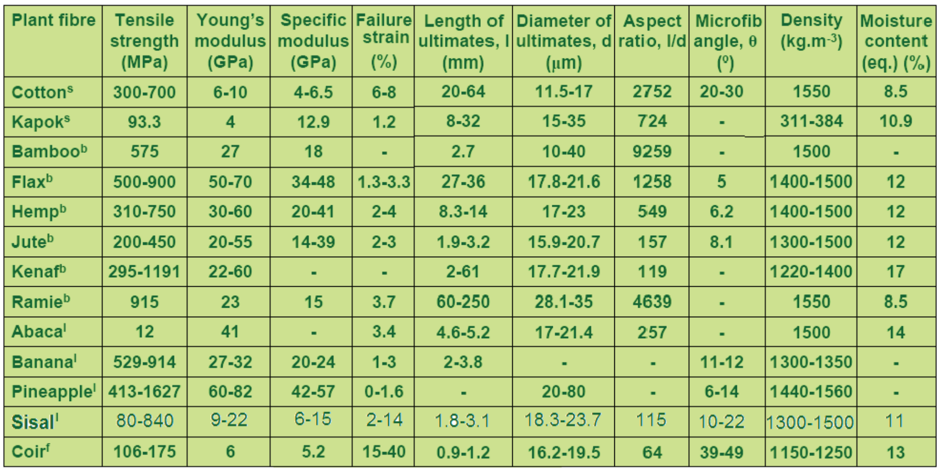


Fig. 6. Embodied energy of flax fibre mat and yarn *(source: ACMC Advanced Composites Manufacturing Centre – University of Plymouth)*

Natural fibres can be classified according to their origin and grouped into *leaf:* abaca, cantala, curaua, date palm, henequen, pineapple, sisal, banana; *seed*: cotton; *bast*: flax, hemp, jute, ramie; fruit: coir, kapok, oil palm. Among them flax, bamboo, sisal, hemp, ramie, jute, and wood fibres are of particular interest (Kalia et als., 2009). The most important physical and mechanical properties are summarized in Table 2.

Physical and mechanical properties depend on the single fibre chemical composition (Cellulose, hemicelluloses, lignin, pectin, waxes, water content and other minors) according to grooving (soil features, climate, aging conditions) and extraction/processing methods conditions. Grooving conditions is recognized as the most influent parameter for the variability of mechanical properties of the fibres. The chemical composition of several natural fibres is summarised in Table 3.



Plant fibre	Tensile strength (MPa)	Young's modulus (GPa)	Specific modulus (GPa)	Failure strain (%)	Length of ultimates, l (mm)	Diameter of ultimates, d (μm)	Aspect ratio, l/d	Microfib angle, θ (º)	Density (kg.m^{-3})	Moisture content (eq.) (%)
Cotton^{s}	300-700	6-10	4-6.5	6-8	20-64	11.5-17	2752	20-30	1550	8.5
Kapok^{s}	93.3	4	12.9	1.2	8-32	15-35	724	-	311-384	10.9
Bamboo^{b}	575	27	18	-	2.7	10-40	9259	-	1500	-
Flax^{b}	500-900	50-70	34-48	1.3-3.3	27-36	17.8-21.6	1258	5	1400-1500	12
Hemp^{b}	310-750	30-60	20-41	2-4	8.3-14	17-23	549	6.2	1400-1500	12
Jute^{b}	200-450	20-55	14-39	2-3	1.9-3.2	15.9-20.7	157	8.1	1300-1500	12
Kenaf^{b}	295-1191	22-60	-	-	2-61	17.7-21.9	119	-	1220-1400	17
Ramie^{b}	915	23	15	3.7	60-250	28.1-35	4639	-	1550	8.5
Abaca^{l}	12	41	-	3.4	4.6-5.2	17-21.4	257	-	1500	14
Banana^{l}	529-914	27-32	20-24	1-3	2-3.8	-	-	11-12	1300-1350	-
Pineapple^{l}	413-1627	60-82	42-57	0-1.6	-	20-80	-	6-14	1440-1560	-
Sisal^{l}	80-840	9-22	6-15	2-14	1.8-3.1	18.3-23.7	115	10-22	1300-1500	11
Coir^{f}	106-175	6	5.2	15-40	0.9-1.2	16.2-19.5	64	39-49	1150-1250	13

Table 2. Natural fibre properties. Source: Natural fibre'09 Proceedings (Universi ty of Bath)

%	Jute	Flax	Hemp	Kenaf	Sisal	Cotton
Cellulose	61-71	71-75	70,2-74,4	53-57	67-78	82,7
Hemicellulose	13,6-20,4	18,6-20,6	17,9-22,4	15-19	10-14,2	5,7
Lignin	12-13	2,2	3,7-5,7	5,9-9,3	8-11	-
Pectin	0,2	2,2	0,9	-	10	-
Others	-	3,8	6,1	7,9	1	-
Waxes	0,5	1,7	0,8	-	2,0	0,6
Water	12,6	10,0	10,8	-	11,0	-

Table 3. Natural fibre composition (Williams et als., 2000; Bogoeva-Gaceva et als., 2007)

Natural fibre mechanical properties depends on the type of cellulose and the geometry of the elementary cell. The celluloses chains are arranged parallel to each other, forming bundles each containing forty or more cellulosic macromolecules linked by hydrogen bonds and through links with amorphous hemicelluloses and lignin which confer stiffness to fibre called microfibrils. More interwoven microfibrils form a rope-like structure (Rong at als., 2001) (Fig.7).

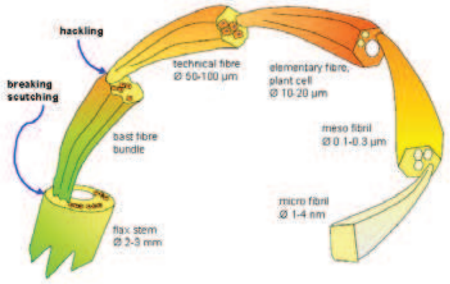


Fig. 7. Natural fibre structure

Among natural fibres the bast fibres, extracted from the stems of plants such as jute, kenaf, flax, ramie and hemp are widely accepted as the best candidates for reinforcements of composites due to their good mechanical properties. Hemp was shown to have very promising tensile properties for applications where mechanical properties are a requisite (Nair at als., 2000)

As many authors agree, the two basic parameters that allow to characterize mechanical behavior of natural fibers are the cellulose content and the spiral angle. In general, the tensile strength of the fibers increases with increasing cellulose content and with decreasing angle of helix axis of the fibers.

The strength of natural fibre composites in on average lower compared to the synthetic fibre reinforced composites, even under optimised fibre-matrix interaction (Heijenrath & Peijs, 1996, Berglund & Ericson, 1995), but their lower density and cost make them competitive in terms of specific and economic properties. This is basically due to the composite-like structure of natural fibres (Van den Oever et als., 1995); they are generally not single filaments as most manmade fibres but they can have several physical forms, which depend on the degree of fibre isolation. Composite strength depends also on fibre diameter (smallest diameter could achieve higher mechanical resistance due to larger specific contact surface with matrix) and fibre length.

1.2 Natural fibre fabric types

The possibility to have long or short fibres depends on the material under consideration, in fact, for synthetic fibre it is easy and common to have long continuous fibres out of production plant, while, for natural fibres, the fibre's length is an inherent limit for the material itself due to their natural origin which limits their length (for example the plant stem). This is a basic reason why natural fibres are usually found as short reinforcements which are used to produce mat fabrics. Discontinuous fibres (*chopped*) are generally used for a randomly oriented reinforcement (*mat*) when there is not any preferential stress direction and/or there is a low stress/strain level in the composite (Fig.8). As it will be shown in the case studies mats, due to the random fibre orientation, are non-optimised fabric for mechanical performances.

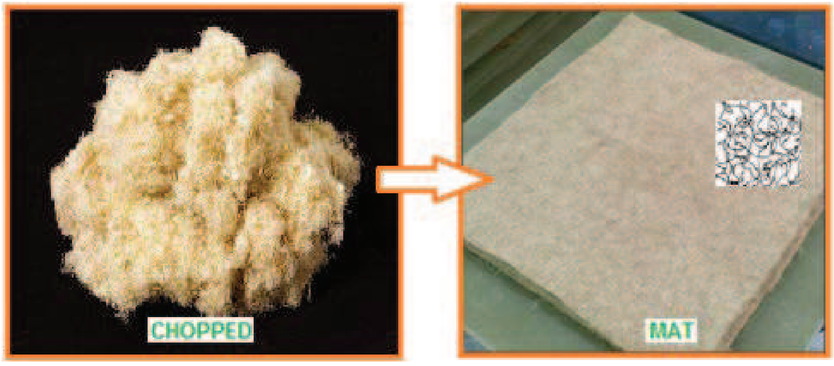


Fig.8. Hemp mat

The alternative to the use of short fibres is the manufacture of long yarns. Yarn is a long continuous assembly of relatively short interlocked fibres, suitable for use in the production of textiles, sewing, crocheting, knitting, weaving, embroidery and ropemaking that are twisted with an angle to the yarn axis in order to provide axial strength to the yarn. Spun yarns are made by twisting or otherwise bonding staple fibres together to make a cohesive thread and may contain a single type of fibre or a blend of various types. Two or more spun yarns, if twisted together, form a thicker twisted yarn. Depending on the direction of this final twist, the yarn will be known as s-twist or z-twist (Fig.9). Two or more parallel spun yarns can form a *roving*. The main advantage of using natural yarns is the possibility to weave them into 2D and 3D fabrics with tailored yarn orientations.

A common measure unit used to classify fibres and yarns is the *denier* which corresponds to the linear mass density of the yarns. Denier is defined as the mass in grams per 9000 meters. In the International

System of Units the tex is used instead, defined as the mass in grams per 1000 meters. The most commonly used unit is actually the decitex, abbreviated dtex, which is the mass in grams per 10000 meters. Similar to tex and denier, yield is a term that helps describe the linear density of a roving of fibres. However, unlike tex and denier, yield is the inverse of linear density and is usually expressed in yards/lb. Linear mass of twisted yarn is expressed by a fraction where the numerator is the yarn count and the denominator is simply the number of ends (e.g. 30/3).

Fig. 9. Hemp twisted yarn and scanning electron microscope image of hemp twisted yarn.

Spun yarns obtained from natural fibres present usually some short fibres protruding out of the main yarn body (Fig.10). This short fibres are commonly referred to as yarn hairiness. Although not desirable in many cases, the hairiness can lead to better mechanical yarn/resin interlocking in composites. Another advantage of natural yarns is the increased surface roughness of yarns compared to fibres, which increases the interfacial strength due to mechanical interlocking, improving the transverse properties. In addition, twisting localizes the micro damages within the yarn leading to higher fracture strength.

Fig. 10. Hemp and flax fibre rovings

An important control parameter for such natural yarns is the twist level. It has been shown (Goutianos & Peijs , 2003) that very low twisted yarns display a very low strength when tested in air and therefore they cannot be used in processes such as pultrusion or textile manufacturing routes like knitting or weaving.(Fig.11) where heavy loading is experienced by the yarns while processing. In the case of short staple (length) fibres, higher twist level is necessary to prevent fibre slippage and to develop sufficient strength.

Besides yarn strength, the amount of twist also affects the inter-yarn impregnation while fabricating reinforced composites. With increased twist level yarns become more compact making it difficult for the resin to penetrate into the yarn. Dry yarns lead to lower bonding between yarns and resin thus leading to delamination and lowering of the composite tensile properties. Several authors showed that when highly twisted yarns are impregnated in a polymer resin, their strength may decrease significantly with decreases similar to the drop in strength of an off-axis composite (Goutianos & Peijs , 2003; Baley, 2002). Thus, there is an optimum level of twist, which should be kept as low as possible for optimal composite mechanical properties to allow for proper yarn's wetting to be achieved.

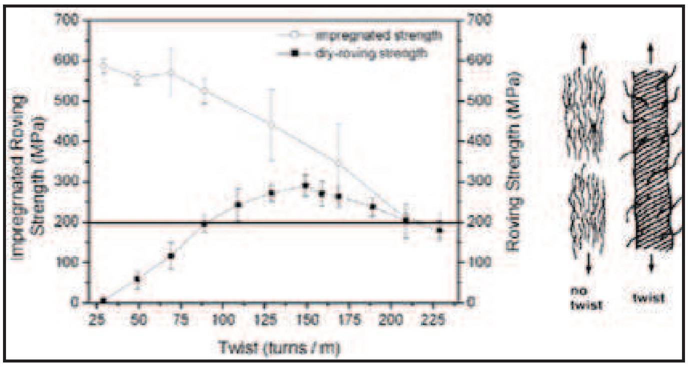


Fig. 11. Effect of twist level on mechanical properties (Goutianos at als., 2006)

The fibre contribution to composite mechanical properties improvement is emphasized when the stresses have components along the fibre direction (Fig. 12). However, most of the studies reported in literature are focused on the use of mat which are the cheapest alternative (Paiva et als., 2004) among technical fabrics. Several studies showed that the random orientation of the fibres in mat fabrics leads to lowering of the reinforcing efficiency (Baiardo et als., 2004).

Yarns offer a viable and interesting alternative to the use of short fibres as multiple filament yarns can be weaved into 2- or 3-Dimension textiles. Weaving is a textile production method which involves interlacing a set of longer threads, twisted yarn or roving, (called the warp) with a set of crossing threads (called the weft) (Fig.13). This is done on a frame or machine known as a loom, of which there are a number of types. Some weaving is still done by hand, but the vast majority is mechanised. The main advantage of using weaved fabrics is the possibility to pre-orient the filaments in the designed directions. Natural yarns differ from multifilament of synthetic fibres (ie.tow) because they are an assembly of short fibre instead of an assembly of aligned continuous fibres. However, the fibres which constitute the yarn have a preferential orientation along an helical trajectory which make the use of natural yarns attractive compared to short fibres because in such yarns fibres are mostly along the load direction.

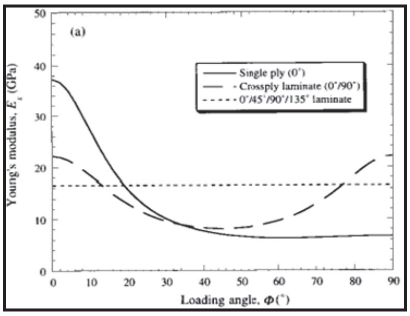


Fig. 12. Effect of fibre orientation on elastic modulus. Data for 50% fibre volume fraction of glass-epoxy laminate (source: Hull & Clyne)

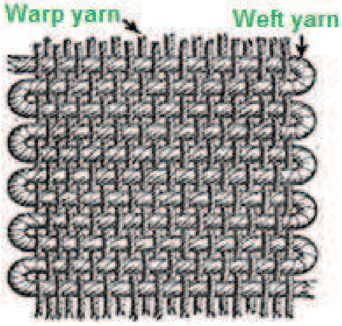


Fig.13. Warp and weft in plain weaving

The manner in which the warp and weft threads are interlaced is known as the *weave style*. The three basic weaves styles or architectures are:

- plain weave
- satin weave
- twill weave

Plain weave is the most basic type of textile weaves.The warp and weft are aligned so they form a simple criss-cross pattern. Each weft thread crosses the warp threads by going over one, then under the next, and so on (Fig.14, 15). The next weft thread goes under the warp threads that its neighbour went over, and vice versa. In balanced plain weaves the warp and weft are made of threads of the same weight (size) and the same number of ends per inch.

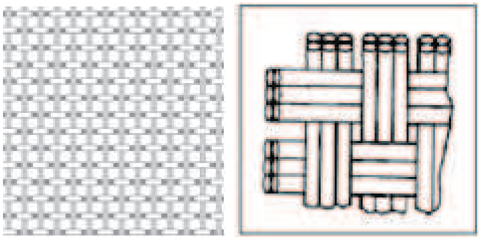


Fig.14. Plain woven yarn and woven roving schemes (0°/90° reinforcement directions)

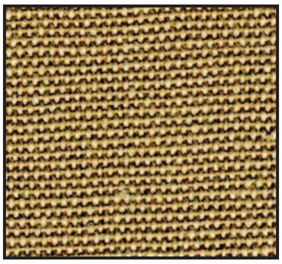


Fig. 15. Examples of plain woven flax yarns. H-181 100% Hemp Canvas weave 18oz/sq yd Wide 59" 5N/2 x 8N/2 x23x21. *Source: dongpinghemp.com*

The satin weave is characterized by four or more weft yarns floating over a warp yarn or vice versa, four warp yarns floating over a single weft yarn (Fig.16).

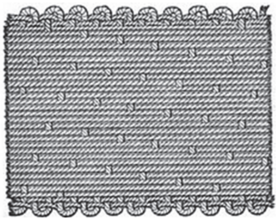


Fig. 16. Satin weave with 16 warp yarns floating over each weft yarn.

Twill is a type of fabric woven with a pattern of diagonal parallel ribs. It is made by passing the weft thread over one or more warp threads and then under two or more warp threads and so on, with a "step" or offset between rows to create the characteristic diagonal pattern (Fig.17,18). Because of this structure, twills generally drape well. In a twill weave, each weft or filling yarn floats across the warp yarns in a progression of interlacings to the right or left, forming a distinct diagonal line. This diagonal line is also known as a wale. A float is the portion of a yarn that crosses over two or more yarns from the opposite direction.

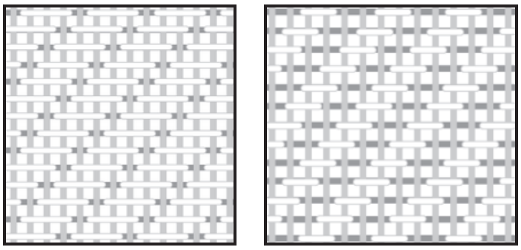


Fig. 17. Structure of a 3/1 and 2/2 twills

A twill weave can easily be identified by its diagonal lines. and is often designated as a fraction—such as 2/1—in which the numerator indicates the number of harnesses that are raised, in this example, two, and the denominator indicates the number of harnesses that are lowered when a filling yarn is inserted, in this example one. The fraction 2/2 would be read as "two up, two down." with two warp threads crossing every two weft threads. The offset at each row forms the diagonal pattern. The minimum number of harnesses needed to produce a twill can be determined by totalling the numbers in the fraction.

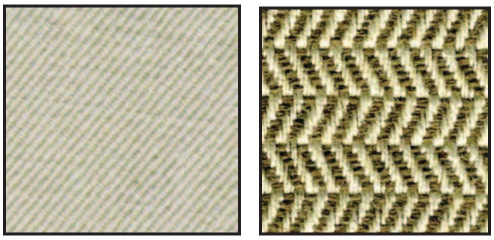
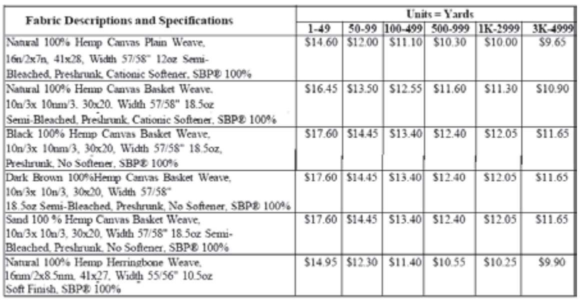


Fig. 18. Examples of plain woven flax yarns. (A) Natural Twill Weave 100% Hemp 12oz Width 57/58" (B) Natural Herringbone Weave 52% Hemp 48% Flax 20oz Width 57/58". ***Source: EnviroTextile.com***

The fewer interlacings in twills allow the yarns to move more freely, and thus they are softer and more pliable, and drape better. Twills also recover better from wrinkles than plain-weave fabrics. When there are fewer interlacings, yarns can be packed closer together to produce high-count fabrics.

There is an increasing number of producers of natural fibre fabrics around the world which are tailoring their products for composites technology. Table 4 shows some costs for a selection of fabrics commercialized in U.S.A. by the company EnviroTextile LLC.



Fabric Descriptions and Specifications	Units = Yards					
	1-49	50-99	100-499	500-999	1K-2999	3K-4999
Natural 100% Hemp Canvas Plain Weave, 16n/2x7n, 41x28, Width 57/58" 12oz Semi-Bleached, Preshrunk, Cationic Softener, SBP® 100%	$14.60	$12.00	$11.10	$10.30	$10.00	$9.65
Natural 100% Hemp Canvas Basket Weave, 10n/3x 10nm/3. 30x20. Width 57/58" 18.5oz Semi-Bleached, Preshrunk, Cationic Softener, SBP® 100%	$16.45	$13.50	$12.55	$11.60	$11.30	$10.90
Black 100% Hemp Canvas Basket Weave, 10n/3x 10nm/3, 30x20, Width 57/58" 18.5oz, Preshrunk, No Softener, SBP® 100%	$17.60	$14.45	$13.40	$12.40	$12.05	$11.65
Dark Brown 100%Hemp Canvas Basket Weave, 10n/3x 10n/3, 30x20, Width 57/58" 18.5oz Semi-Bleached, Preshrunk, No Softener, SBP® 100%	$17.60	$14.45	$13.40	$12.40	$12.05	$11.65
Sand 100 % Hemp Canvas Basket Weave, 10n/3x 10n/3, 30x20, Width 57/58" 18.5oz Semi-Bleached, Preshrunk, No Softener, SBP® 100%	$17.60	$14.45	$13.40	$12.40	$12.05	$11.65
Natural 100% Hemp Herringbone Weave, 16nm/2x8.5nm, 41x27, Width 55/56" 10.5oz Soft Finish, SBP® 100%	$14.95	$12.30	$11.40	$10.55	$10.25	$9.90

Table 4. Natural fibre fabrics sold by EnviroTextile

Other examples of commercial products available on the market are the flax fabric (Fig. 19) manufactured by Biotex (http://www.compositesevolution.com) which are also available as pre-impregnated fabric with PLA (polylacticacid) and PP (polypropylene). Other products available are the pre-impregnated fabrics (FLAXPLY©) produced by Lineo. The products sold by Lineo have pre-treated fibers for increased fiber-matrix adhesion. The FLAXPLY© are proposed to be used for internal layer of mixed carbon/flax design for improved vibration absortion (Fig.20).

As mentioned before, yarns and rovings can be weaved in 3-Dimension fabrics, even if they are not so widespread as plain ones. To date no commercial example of 3D weaved fabric based on natural yarns is available.

Fig. 19. Biotex Flax 3H Satin 420gsm

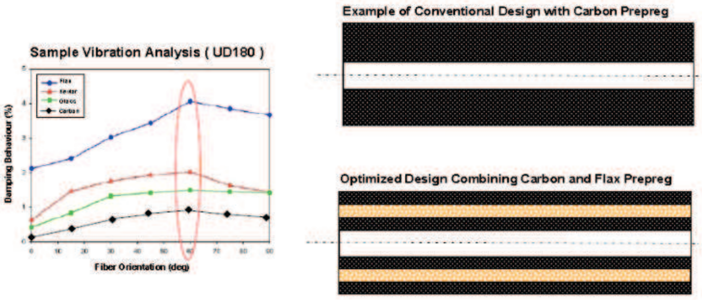


Fig. 20. Example of the use of FLAXPLY© for vibration absorption

1.3 Fiber surface treatments

The contribution of fibres to the final properties of the composite depends on:

- Mechanical properties of fibres;
- Type (continuos/discontinuos) and orientation of fibres in the composite (anisotropy).
- Volume fraction of fibres;
- Fibre-matrix interface;
- Processing technique used for composite manufacturing.

Shortcomings associated with natural fibres have to be overcome before using them in polymer composites. The most serious concern with natural fibres is their hydrophilic nature due to the presence of pendant hydroxyl and polar groups in various constituents, which can lead poor adhesion between fibres and hydrophobic matrix polymers (Rong et als., 2001, Bledzki & Gassan, 1996). The hydrophilic nature of the fibre surface lead also to high moisture up take for the natural fibres which can seriously lower the mechanical properties of the fibres themselves.

The natural fibres are inherently incompatible with nonpolar-hydrophobic thermoplastics, such as polyolefins. Moreover, difficulty in mixing because of poor wetting of the fibres with the matrix is another problem that leads to composites with weak interface (John & Anandjiwala, 2008).

There are some physical fibre treatments (e.g Plasma), but nowadays when we speak about surface treatments we almost mean chemical ones. These treatments can clean the fibre surface, modify the chemistry on the surface, lower the moisture up take and increase the surface roughness. As the natural fibres bear hydroxyl groups from cellulose and lignin they are amenable to chemical modification. The hydroxyl groups may be involved in the hydrogen bonding within the cellulose molecules thereby reducing the activity towards the matrix. Chemical modifications may activate these groups or can introduce new moieties that can effectively lead to chemical interlock with the matrix. Mercerization, isocyanate treatment, acrylation, permanganate treatment, acetylation, silane treatment and peroxide treatment with various coupling agents and other pretreatments of natural fibres have achieved various levels of success for improving fiber strength, fiber fitness and fiber-matrix adhesion. In the following section we report a review of the main preteatments techniques.

1.4 Alkali treatment

Alkali treatment of natural fibers, also called mercerization, is the common method to produce high-quality fibers. The scheme of the reaction is:

$\text{FIBER-OH} + \text{NaOH} \rightarrow \text{FIBER-O}^{-}\text{Na}^{+} + H_2O$.

Mercerization leads to fibrillation which causes the breaking down of the composite fibre bundle into smaller fibres. Mercerization reduces fibre diameter, thereby increases the aspect ratio which leads to the development of a rough surface topography that results in better fibre/matrix interface adhesion and an increase in mechanical properties (Kalia at als., 2009). Moreover, mercerization increases the number of possible reactive sites, allows better fibre wetting and gets an effect on the chemical composition of the hemp fibres, degree of polymerization and molecular orientation of the cellulose crystallites due to cementing substances like lignin and hemicelluloses which were removed during the mercerization process. As a result, mercerization had a long-lasting effect on the mechanical properties of hemp fibres, mainly on fibre strength and stiffness. If the treatment is done at high percentage of NaOH there could be an excessive extraction of lignin and hemicelluloses which can results in damage of the ultimate cells walls. Similar reduction of mechanical properties after alkali treatment have been reported in the literature (Rodriguez at als., 2007).Alkali treatment is recognized to hydrolyses the amorphous parts of cellulose present in fibres so that after treatment the material contains more crystalline cellulose (Le Troedec, 2008). Furthermore, it removes waxes and oils from the surfaces (Sgriccia, 2008).

1.5 Acetylation

Acetylation was originally applied to wood cellulose to stabilize the cell walls against moisture, improving dimensional stability and environmental degradation and to introduce plasticization to cellulosic fibers by esterification. Acetylation is based on the reaction of cell wall hydroxyl groups of lignocellulosic materials with acetic or propionic anhydride at elevated temperature (Fig.21). Pretreatment of fibers with acetic anhydride substitutes the polymer hydroxyl groups of the cell wall with acetyl groups, modifying the properties of these polymers so that they become hydrophobic (Andersson & Tillman, 1989; Murray, 1998; Rowell, 1991) Hydroxyl groups that react with the reagent are those of lignin and hemicelluloses (amorphous material), whereas the hydroxyl groups of cellulose (crystalline material) are being closely packed with hydrogen bonds, prevent the diffusion of reagent and thus result in very low extents of reaction (Rowell, 1998).

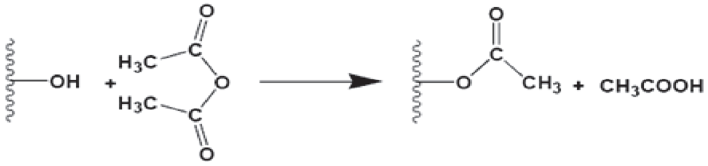


Fig. 21 Scheme of acetylation reaction

1.6 Peroxide treatment

Peroxide treatment of cellulose fibre has attracted the attention of various researchers due to easy processability and improvement in mechanical properties. Organic peroxides tend to decompose easily to free radicals, which further react with the hydrogen group of the matrix and cellulose fibers. In peroxide treatment, fibers are treated with 6% benzoyl peroxide or dicumyl peroxide in acetone solution for about 30 min after alkali pretreatment (Sreekala at als., 2002; Sreekala et als., 2002; Paul et als., 1997) conducted at a temperature of 70°C to support the decomposition of the peroxide.

1.7 Graft copolymerization

Synthesis of graft copolymers by creation of an active site, a freeradical or a chemical group which may get involved in an ionic polymerization or in a condensation process, on the preexisting polymeric backbone is one of the common methods. Polymerization of an appropriate monomer (e.g. benzoyl chloride, maleated polypropylene/maleic anhydride MAH-PP, acrylation, titanate) onto this activated back-bone polymer leads to the formation of a graft copolymer with a higher surface energy and wettability and adhesion interface by polymer matrix. It has been reported that maleic anhydride treatment reduced the water absorption to a great extent in hemp, banana and sisal fibers and their composites (Mysra et als.2000).

Modification of cellulosic fibers by etherification enhances certain new ranges of properties and makes it more useful and acceptable in diversified applications. Sodium hydroxide plays an important role in forming a charged intermediate species with the fiber, which allows the faster nucleophilic addition of epoxides, alkyl halides, benzyl chloride, acrylonitrile, and formaldehyde (Matsuda, 1996).

Benzoyl chloride is the most often used benzoylation pretreatment. Benzoyl ($C_6H_5C{=}O$) groups react with the cellulosic OH group of fiber decreasing hydrophilic nature of the treated fiber (Joseph et als., 2000) after a 30 min pre-soaking with NaOH solution to activate the hydroxyl groups of the cellulose and lignin in the fiber, followed by filtration and washing with water (Fig.22).

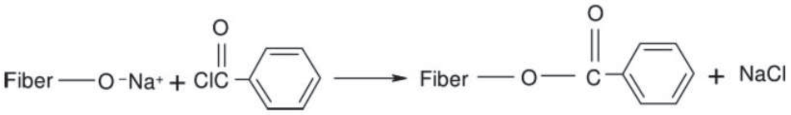


Fig. 22 Possible reaction between cellulosic-OH and benzoyl chloride (Joseph et als., 2000)

A number of methods can be used for the generation of active sites on the polymeric backbone and can be described as: physical, chemical, physicomechanical, radiation method and enzymatic grafting. The conventional techniques of grafting of natural fibers require significant time and energy. It has been found that grafting under microwave radiations is the best method in terms of time consumption and cost effectiveness. Microwave radiation technique reduces the extent of physicochemical stresses to which the fibers are exposed during the conventional techniques (Kaith & Kalia 2008).

1.8 Coupling agents

Coupling agents usually improve the degree of crosslinking in the interface region and offer a perfect bonding. Among the various coupling agents, silane coupling agents were found to be effective in modifying the natural fiber-matrix interface. Silane grafting is based on the use of reactancts that bear reactive end groups which, on one end, can react with the matrix and, on the other end, can react with the hydroxyl groups of the fiber (Fig.23). The alkoxy or ethoxy are the end groups which can form stable covalent bonds reacting with the hydroxyl groups of the fiber. The end groups which can react with the matrix vary according to the polymer matrix type. If unsaturated polyester is used silanes bearing methacryl-, amine- and vinyl- can be used (Soo-Jin et als., 2001; Li Hu at als., 2009). Efficiency of silane treatment was high for the alkaline treated fiber than for the untreated fiber because more reactive site can be generated for silane reaction. Therefore, fibers are pretreated with NaOH for about half an hour before its coupling with silane. Fibers are then washed many times in distilled water and finally dried. Silane coupling agents may reduce the number of cellulose hydroxyl groups in the fiber-matrix interface minimizing fibre sensitivity to humidity. In the presence of moisture, hydrolizable alkoxy group leads to the formation of silanols. The silanol then reacts with the hydroxyl group of the fiber, forming stable covalent bonds to the cell wall that are chemisorbed onto the fiber surface (Agrawal et als., 2000). Therefore, the hydrocarbon chains provided by the application of silane restrain the swelling of the fiber by creating a cross-linked network because of covalent bonding between the matrix and the fiber.

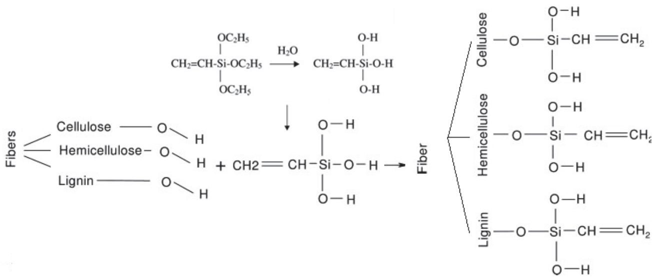


Fig. 23 Reaction of silane with OH groups of natural fiber

Silanes are effective in improving the interface properties (Coutinho at als., 1997; Gonzales et als., 1997). Alkoxy silanes are able to form bonds with hydroxyl groups. Fiber treatment with toluene dissocyanate and triethoxyvinyl silane could improve the interfacial properties. Silanes after hydrolysis undergo condensation and bond formation stage and can form polysiloxane structures by reaction with hydroxyl group of the fibers. Silane grafting can modify the mechanical performances of fiber as a consequence of the use of acid solution for the treatment.

Isocyanate has –N=C=O functional group, which is very susceptible to reaction with the hydroxyl group of cellulose and lignin in the fibers and forms strong covalent bonds, thereby creating better compatibility with the binder resin in the composites (Kokta et als. 1990).

1.9 Permanganate treatment

Pretreatments with permanganate are conducted by using different concentration of potassium permanganate ($KMnO_4$) solution in acetone with soaking duration from 1 to 3 min after alkaline pretreatment. As a result of permanganate treatment, the hydrophilic tendency of the fibers is reduced, and thus, the water absorption of fiber-reinforced composite decreases with increase in $KMnO_4$ concentration (Sreekala et als., 2000; Paul et als., 1997). Permanganate treatment is indicated as one of the best method to improve the bonding at the fiber-polymer interface.

1.10 Physical plasma treatment

Plasma treatment is an effective method to modify the surface of natural polymers without changing their bulk properties. The plasma discharge can be generated by either corona treatment or cold plasma treatment. Both methods are considered as a plasma treatment when ionized gas has an equivalent number of positive and negative charged molecules that react with the surface of the present material. The distinguishing feature between the two categories of plasmas is the frequency of the electric discharge. High-frequency cold plasma can be produced by microwave energy, whereas a lower frequency alternating current discharge at atmospheric pressure produces corona plasma. The type of ionized gas and the length of exposure influenced the modification of the wood and synthetic polymer surfaces (Young et als., 1992; Goring & Bolam, 1976).

1.11 Chemical treatments on natural fibre: effect on mechanical properties

Chemically treated fibers can show a considerable decrease in tensile properties and this decrease is attributed to the substantial delignification and degradation of cellulosic chains during chemical treatment. The extension at break of these fibers does not change much. Most of the chemical treatments have been found to decrease the fiber strength due to breakage of the bond structure, and disintegration of the noncellulosic materials but silane and acrylation treatment leave to strong covalent bond formation and the stiffness is enhanced marginally due to the crystalline region (cellulosic) of the fiber.

The alkali treatment can produce a drop in both tensile strength and Young's modulus of the fibers if a very high percentage treatment is adopted. This result is attributed to the damage induced in the cell walls and the excessive extraction of lignin and hemicellulose, which play a cementing role in the structure of the fibers.

Morphological studies showed that the silane, benzoylation and peroxide pretreatment of flax fiber improved the surface properties. Silane and peroxide treatment of flax led to a higher tensile strength than that of untreated flax (Wang et als., 2007).

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Chapter 2 Wood Plastic Composite

New generation wood–plastic composites (WPCs) are an environmental-friendly green material created from the ‘‘marriage’’ of the forestry and plastic industries [1-2].

The term wood plastic composite (WPC) refers to any composite material that contains wood and thermoplastics (Fig.3). WPC products have commonly substituted for solid wood in today’s building structures over the last decade. The objective of WPC development is to produce a product with performance characteristics that combine the positive attributes of wood and plastic. Significant advantages of WPC are their high durability and renewability, low maintenance, acceptable relative strength and stiffness, less abrasive wear to processing equipment, environmental friendly, and similar as wood feature [3].

Figure 3 Wood plastic composite

This type of new materials differ from the conventional wood–plastic products, which were mainly composed of virgin thermosetting resins (i.e. phenol- or melamine-formaldehyde resin) and different types/shapes of woods (i.e. sheets, particles, or fibers), and can be manufactured by using recycled wood flour (WF) and recycled plastic resins. Additional values can be created and the service life of wood products can be extended, resulting in significant reduction in environmental impacts and carbon footprint of the waste materials [4]. Furthermore, WPCs have many unique properties which differ significantly from the original materials: WFs can provide physical support to the plastic matrix and increase the mechanical strengths (i.e. stiffness) of the products [5]. Although the biological resistance of WPCs is not as superior as believed by the conventional wisdom, the plastic matrix do can provide protection to the wood fiber from moisture: if the wood fiber and plastic can be properly bounded through coupling agents and suitable wood/plastic combination, the resistances of WPCs to water absorption and thickness swelling can be significantly improved. WPCs have found applications in many areas, i.e. automotive industries, windows, doors, and decking [6-7].

WPCs have also been widely used in outdoor applications, i.e. public facilities, and industrial or recreational purposes. When applied in the outdoor environment, however, different weathering conditions, i.e. sunlight exposure, rainfall, changes in humidity and/ or temperature, could considerably affect the durability of WPCs. Wood is a biomaterial with which the physical and mechanical properties can be significantly affected by the ambient conditions, especially when the plastic matrix cannot completely cover the wood fibers.

Wood-plastic composites combine the best properties of the neat components and can show outstanding performance. Wood flour is a readily available and relative inexpensive filler that can lower resin costs, improve stiffness, and act as an environmentally friendly way to reduce the use of petroleum-based plastics. In addition, WPCs have the advantages of good dimensional stability during lifetime, i.e. lower water uptake, and durability against fungi and insects compared with wood [8].

Wood flour (WF) is gaining more and more acceptance as a kind of filler for polymers due to its low density, easy availability, biodegradation, high stiffness, renewability and relatively low cost. In addition, the renewable and biodegradable characteristics of wood fibers facilitate their ultimate disposal by composting or incineration. According to the advantages of wood fiber, the production of wood plastic composites (WPCs) and its application in many areas has attracted much attention in the past ten years. They were used in interior decoration and construction industries such as decking, railing, fencing, docks, landscaping timbers, and in a number of automobile industries. However, when combining thermoplastics with wood fibers by conventional methods, the highly hydrophilic characters of the lignocelluloses materials make them incompatible with the thermoplastics which are highly hydrophobic. The incompatibility leads to poorer interfacial adhesion between thermoplastics and wood filler, and worse of the composite properties. In addition, the hydroxyl groups between wood fibers can form hydrogen bonds which can lead to agglomeration the fibers into bundles and unevenly distribution throughout the non-polar polymer matrix during the compounding processing. However, the WF is mainly made of cellulose, hemicelluloses, lignin and pectins, which leads to water absorption of the WPC resulting in debonding fibers and degradation of the fiber–matrix interface. In addition, the high moisture absorption of natural fibers may cause dimensional change of the resulting composite and weakened the interfacial adhesion.

However, there are mainly two drawbacks for WPCs. Adhesion between wood flour and thermoplastics, especially for non-polar resin such as polypropylene (PP), is not enough to improve the mechanical properties. The addition of MAPP can overcome the week adhesion property. The other disadvantage is that the WPCs show high flammability. High flammability of WPCs sets a limit to the application field of WPCs [9-11].

2.1 Beginning and history of WPC

The first WPC, in the 1960s, were thermosetting molding compounds containing cellulose fiber as filler.

Earlier attempts, in the 1970s, to make cellulose-filled thermoplastic compositions had identified a serious obstacle. It became recognized that fillers, particularly cellulose fibers, do not disperse easily throughout the plastic formulations during compounding and molding. Accordingly, the finished products typically do not exhibit the desirable physical characteristics ordinarily associated with fiber reinforced plastic composites.

In the 1980s, more attention has been increasingly paid to improving the physical properties, such as mechanical strength, stiffness, resistance to thermal deformation, and so forth, of the fiber–plastic composite products. It was recognized that moisture in cellulosic fiber leads to steam formation in the compounder and the extruder, increases porosity of the final product and decreases its density, accelerates the oxidation of the hot melt during processing, and makes the final product weaker and less durable.

Attention has also been paid to improving the compatibility of the filler with the polymer matrix, by providing an interaction between the filler and the polymer. “Compatibilizers” can be chemically attached either to cellulose fibers, or to a polymer, or can form a covalent chemical bond between the two, or can help to form a sort of uniform “alloy” between two or several polymeric components ordinarily not very compatible with each other. Or compatibilizers can improve adhesion between fiber and plastic by other means. Generally, compatibilizers markedly improve physical properties of the polymeric composite, its weatherability, and overall performance.

Attention in 1990s was paid to alternative thermoplastic materials (e.g., other than polyethylene).

Another innovation in the 1990s involved compounding thermoplastic polymers and cellulosic materials along with other ingredients into a feedstock in the form of durable, easy to transport, and durable pellets. A new and a challenging direction in making composite materials more lightweight and economical became visible by the middle of the 1990s. Foaming was, of course, well known in neat plastic materials, particularly having a high melt strength. A high content of cellulose fiber in plastics, particularly in polyethylene, makes the composite material much less suitable for foaming and significantly decreases the composite’s flexural strength and flexural modulus. Therefore, foaming of WPC often requires reinforcing, coupling agents, or employing a strong plastic, such as PVC [12].

2.2 Biodegradable Wood–Plastic Composites

Ultimately, all WPCs are degradable and biodegradable in the grand scheme of time.

This is particularly related to WPCs, having low amounts of antioxidants.

"Biodegradable" WPCs are composites specially designed to have a short lifetime outdoors, especially when disposed of after the end of their intended service. Often, biodegradable WPCs are made for indoor applications, such as flooring.

It should be noted that although the developments include various thermoplastic composites based on waste materials, few of these materials are readily available on a widespread and cost-effective basis. Moreover, their proportion in the overall composite mixture tends to be somewhat low, because high proportions of non-plastic components can compromise mechanical properties [12]. As a result, the environmental benefits offered by these compositions are limited.

Biodegradable plastics, such as polylactic acid, are considered by many as a promising direction in WPC, mainly for interior applications.

2.3 Description of wood fibers

Throughout history, the unique characteristics and abundance of wood have made it an attractive choice for different applications when using natural materials. At present, wood fiber-reinforced thermoplastics are enjoying rapid growth because of a number of advantages. Wood elements, used in polymer composites , have a large variety of shapes and can be used alone or in combination [13-14]. Wood particles, such as chips, flakes, fibers, and wood pulps are used as reinforcing agents. The fibrous nature of wood strongly influences how it is and can be used. Wood is primarily composed of hollow, elongate, spindle-shaped cells that are arranged parallel to each other along the trunk of the tree. When lumber and other products are cut from the tree, the characteristics of these fibrous cells and their arrangement affect properties such as strength and shrinkage as well as the pattern of the wood. Woods are divided into two broad classes, usually referred to as hardwoods (HWs) and softwoods (SWs). This classification can be quite confusing since some SWs are actually harder than some HWs and, conversely, some HWs are softer than some SWs [15].

2.4 Modification of wood fibers

At present, WPCs are being developed that could benefit from a thorough and fundamental understanding of the fiber surface. These products may require new adhesive systems to reach their full commercial potential. The wood floor surface is a complex heterogeneous polymer composed of cellulose, hemicelluloses, and lignin. The surface is influenced by its polymer morphology, extractive chemicals, and processing conditions. The extent of the fiber-matrix interface is significant for the application of wood fibers as reinforcement fibers for plastics. An exemplary strength and stiffness could be achieved with a strong interface that is very brittle in nature with easy crack propagation through the matrix and fiber. The efficiency of stress transfer from the matrix to the fiber could be reduced with a weaker interface [16].

2.4.1 Physical Methods

Reinforced fibers can be modified via physical methods. Physical treatments change structural and surface properties of the fiber and thereby influence the mechanical bonding of polymers. Physical treatments do not extensively change the chemical composition of the fibers. Therefore, the interface is generally enhance d by means of increased mechanical bonding between the fiber and the matrix.

2.4.2 Corona treatment

Corona treatment is one of the most interesting techniques for surface oxidation activation. This process changes the surface energy of the cellulose fibers. Corona discharge treatment used on wood fibers and hydrophobic matrices was found to be effective in improving the compatibility between hydrophilic fibers and hydrophobic matrices.

Using corona treatment on wood flour under optimal operating conditions offers the possibility of improving its efficiency as filler for rubber compounds.

2.4.3 Plasma treatment

Plasma treatment is another physical treatment method, similar to corona treatment. The properties of plasma are exploited by this method, in order to induce changes on the surface of a material. A variety of surface modifications can be achieved depending on the type and nature of the gases used. Reactive free radicals and groups can be produced , surface energy can be increased or decreased , and surface cross-linking can be introduced .

2.4.4 Chemical Methods

Wood fibers, which are strongly polarized, are inherently incompatible with hydrophobic polymers because of their hydrophilic nature. In many cases, when two materials are incompatible it is possible to create compatibility by introducing a third material that has transitional properties between those of the other two. There are several mechanisms of coupling in materials.

- *Weak boundary layers*-coupling agents eliminate weak boundary layers.
- *Deformable layers*-coupling agents produce a tough, flexible layer.
- *Restrained layers* - coupling agents develop a highly cross-linked interphase region, with a modulus intermediate between that of the substrate and that of the polymer.
- *Wettability*- coupling agents improve wetting between polymer and substrate (critical surface tension factor).

- Chemical bonding-coupling agents from covalent bonds with both materials.
- Acid - base effect-coupling agents alter acidity of the substrate surface.

The development of a definite theory for the mechanism of bonding achieved with the aid of coupling agents in composites is a complex problem [17-18].

2.5 Matrix for WPC

The WPCs' shape, surface appearance, environmental tolerance, and overall durability are dominated by the matrix, while the fibrous reinforcement carries most of the structural loads, thus giving the composites macroscopic stiffness and strength.

The polymer market is dominated by commodity plastics, while 80% of the consumption of products is based on nonrenewable petroleum resources.

Governments, companies, and scientists seek to find an alternative matrix to the present leading petroleum-based matrix. Their motivation is fueled by public awareness of the environment, climate change, and limited fossil fuel resources. Therefore, biobased plastics have experienced a renaissance in the past decades, which is from renewable resources [19].

2.5.1 Thermoplastics

The lower thermal stability of wood fibers at temperatures up to 230°C limits the number of thermoplastics that can be used as matrix materials for WPCs.

Only those thermoplastics whose processing temperatures do not exceed 230°C are applicable for WPCs. These are generally polyolefines and, nowadays, technical thermoplastics, such as polyamides, polyesters, and polycarbonates. They require processing temperatures > 250°C, are suitable for composite processing when modified, and do not undergo fiber degradation.

2.5.2 Petrochemical-based Thermoplastics

The effect of incorporating wood fibers in a petrolchemical-based thermoplastic matrix such as PE, PP, PVC and PS, was extensively studied.

2.5.3 Bio-Based Thermoplastics

Public concern about the environment, climate change, and limited fossil fuel resources is a key incentive for finding alternatives to crude oil [20].

2.6 Processing of wood plastic composites

The material handling system starts with raw materials and is the first step in manufacturing composites. The material handling system has various components such as receiving and storage, size reduction, and especially, drying. The moisture content of wood has a significant effect on the processing and final product quality of WPCs.

Therefore, drying fibers before processing is an important factor, as water on the fiber surface acts like a separating agent in the fiber-matrix interface. Additionally, during the reaction process, voids appear in the matrix because of the evaporation of water.

Both phenomena lead to a decrease in the mechanical properties of wood fiber-reinforced composites. Fiber drying can be done in a vacuum oven at different temperatures. However, in some cases, moisture can be removed as part of the processing in which additional drying equipment is required . Some available equipment are preheaters, high intensity mixers, hot air dryers, and rotary tube furnace. The various processes for the manufacture of WPC products are compounding, extrusion, and injection molding.

2.6.1 Compounding

Compounding is of key importance for obtaining materials with appropriate processing characteristics. Before WPCs can be processed into a final product, they usually have to undergo compounding. Not only the base materials but also the choice of additives determines the properties of the finished product. Compounding is the process of imparting the desired distribution to two or more components that may be present in solid or liquid form. The fibers and additives are dispersed in the molten polymer to produce a homogeneous blend. The developed available processes for compounding use either a batch (e.g., internal and thermokinetic mixers) or a continuous mixer (e.g. extruders, kneader).The processing parameters (e.g., residence time, shear, and temperature) are easier to control in batch systems, whereas the continuous compounding systems, however, do not have the problem of differences in batch-to-batch quality.

2.6.2 Compression molding

Thermoplastic wood fiber reinforced composites are distinguished from thermoset- reinforced composites primarily by a high elongation at break, short cycle times, and the possibility of recycling. The compression molding process has proved suitable for the production of profiles with any thermoplastic prepreg. Compression molding forms the thermoplastic prepreg gently into the required shape without overcompressing the material. The different layer orientations are thus retained after molding.

2.6.3 Extrusion

The extrusion process is required so as be able to melt the polymer and mix the molten polymer with the wood fiber, thus producing a WPC. By doing so, a homogeneous melt is achieved. The remaining moisture can be removed via vacuum venting. The extruder then compresses the blend , passing it through the die. Processing should not be detrimental to the wood fiber. Single-screw and twin-screw extruders that run co- or counter-rotating, conical, and nowadays coextrusion, is used for WPCs. Single-screw extruders are used when the mixing effect does not have to be very high. As a rule, corotating twin-screw extruders are used in the production of granules (compounding) or in the processing of wood fiber-reinforced plastics. Owing to the excellent mixing effect of the twin -screw extruder, the wood fiber material can be homogenously distributed and wetted in the thermoplastic melt.

The low density state of wood fibers represents a feeding challenge when employed as reinforcements in wood fiber-plastic composites manufactured by extruder-based processing. This challenge has prevented the commercial use of wood fibers as reinforcements in various composite applications.

Twin -screw extruders are widely used for wood fiber-plastic composites, and the large number of patents of wood fiber - plastic composites produced using extrusion processing indicates the speed of commercialization that has taken place.

2.6.4 Injection molding

Using injection molding makes it possible to produce complex geometric components with functional elements fast and in great numbers. Injection molding requires a polymer with a low molecular weight , so as to maintain a low viscosity. By contrast, extrusion requires a polymer with a higher molecular weight for better melt strength. Injection molding offers a number of advantages compared to compression molding, such as economics of scale, minimal warping and shrinkage, possibility of high function integration, the possibility of employing recycling material, and the fact that hardly any finishing is needed. In injection molding, the raw material is usually added as granules to the injection molding machine and melted into a fluid mass . The plasticized thermoplastic material is then injected into the form under high pressure. The reinforcing fibers influence the injection molding process when fiber-reinforced granules are used.

The injection molding process was applied to WPCs regarding the effects of processing methods and fiber sizes on the structure and properties and achievement of improved properties using better processing.

2.6.5 Thermoforming

Thermoforming is a manufacturing process in which a composite sheet is heated to a pliable forming temperature , formed to a specific shape in a mold , and trimmed to create a usable product. The sheet, or "film" when referring to thinner gauges and certain material types, is heated in an oven to a temperature that makes it possible to be stretched into or onto a mold and cooled to a finished shape [12].

2.7 Performance of WPC

2.7.1 Mechanical

There are several mechanical properties that are important to know about each type of wood fiber , so as to be able to make use of the highest potential. Tensile, flexural, impact, dynamic mechanical , and creep properties are among the important properties. In general, wood fibers are suitable for reinforcing plastics because of their relatively high strength and stiffness and their low density.

2.7.2 Tensile Properties

The tensile properties are one of the most widely tested properties of wood fiber- reinforced composites. The fiber strength can be an important factor when selecting a specific wood fiber for a specific application . A tensile test reflects the average property through the thickness, whereas a flexural test is strongly influenced by the properties of the specimen closest to the top and bottom surfaces. The stresses in a tensile test are uniform throughout the specimen cross section, whereas the stresses in flexure vary from zero in the middle to maximum in the top and bottom surfaces.

2.7.3 Flexural Properties

Flexural stiffness is a measure of deformability. The flexural stiffness of a structure depends on two properties: the elastic modulus (stress per unit strain) of the material that composes it and the second moment of inertia, a function of the cross-sectional geometry. Flexural properties are also among the most widely investigated properties, such as tensile properties.

2.7.4 Impact Properties

Impact strength is the ability of a material to resist fracture under stress applied at high speed. Biofiber- reinforced plastic composites have properties that can compete with glass fiber thermoplastic composites , especially when specific properties are considered. However , one property, namely , impact strength, is often listed among the major disadvantages of biofiber-reinforced composites compared to glass fiber thermoplastic composites. In recent years, with the development of new fiber manufacturing techniques and improved composite processing methods, as well as the enhancement of the fiber/matrix adhesion, the situation has improved somewhat.

2.7.5 Physical

When dry, wood fiber has unique properties. Knowledge of water-polymer interactions in polymeric composite materials is critical in order to be able to predict their behavior in applications in which they are exposed to water or humid environments. The application of wood fiber reinforcement is limited mainly because of the changes in geometry caused by swelling.

Drying fibers before processing is of importance because water on the surface acts likes a separating agent in the fiber-matrix interface.

2.7.6 Swelling

The hydroxyl groups (-OH) in cellulose, hemicelluloses, and lignin build a large amount of hydrogen bonds between the macromolecules of the wood polymers.

Exposing the wood to humidity causes these bonds to be break. The hydroxyl groups then form new hydrogen bonds with water molecules, which induce the swelling.

2.7.7 Biological

The largest growing markets of WPC is decking, and it is exposed to moisture, light, temperature changes, freezing, thawing, and biological attacks by fungi and bacteria in outdoor applications.

The biological properties of WPCs depend on the load of wood material in the matrix and on the surface condition of the samples produced . These properties are significantly different from the biological properties of natural components used . The improved spectrum of properties is the basis for the success in the market.

WPCs are sold for exterior application as decay-resistant materials that require no maintenance. The plastic matrix is presumed to protect the fiber or wood particles against biological attack. However, wood particles remain susceptible to fungal degradation since certain amounts of water can be absorbed. In order to prevent potential decaying, borates, such as zinc borate, can be incorporated as effective and leach-resistant preservatives.

2.7.8 Bacterial

Bacteria tend to colonize wood fibers with high moisture content. They can affect wood permeability, attack the structure, and work together with other bacteria or fungi. Lignocellulose degrades in a very slow process. While the bacterial degradation for wood fibers has been thoroughly investigated, literature on the bacterial biodegradation of plastic composites is limited [21-22].

2.8 Uses and Applications

The term *wood-based composite* is used to describe any wood material bonded together with adhesives. The basic wood elements in the production of wood-based composites can be in a great variety of sizes and geometries: fibres, sawdust, shavings, larger particles composed of many fibers, flakes, strands, and veneers. These elements can be used alone or in combination. The choice is almost unlimited. Wood-based composite boards are made from these wood elements in a panel form.

Morphology of the wood elements influences the properties of composite materials, and can be controlled by selection of the wood raw material and by the processing techniques used to generate the wood elements. Composite properties can also be controlled by segregation and stratification of wood elements having different morphologies in different layers of the composite material. In conventional wood-based composites, properties can also be controlled by the use of adhesives with different curing rate in different layers. Varying the physical configuration of the wood element, adjusting the density profile of the composite, adjusting adhesive resin, or adding chemical additives is just a few of the many ways to influence the properties. Wood-based composites are used for a number of structural and non-structural applications including panels for exterior, interior, and furniture used. Performance standards are in place for many conventional wood- based composite products.

Generally, wood-based composites provide uniform and predictable in- service performance, largely as a consequence of standards used to monitor and control their manufacturing process. The mechanical properties of wood composites depend on a variety of factors, including wood species, forest management regimes (naturally regenerated, intensively managed), the type of adhesive, geometry of the wood elements (fibres, flakes, strands, particles, veneer, lumber), and density of the final product.

Wood-plastic composites (WPCs) belong to the well-known established material and have experienced a significant gain in application over the past decade. WPCs are under development for and are currently being used in a wide range of applications in a number of market sectors: building and construction, automotive sector, interiors and internal finishes, garden and outdoor products, industrial products and infrastructure, and other low volume niche applications. The list of areas of application is seemingly endless and continues to expand with products such as decking, railing, fencing, roofing, automotive interior panels, automotive door and head liners skirting boards, etc.

The consumer acceptance of these products will be driven by the fact they act as replacements for the more traditional materials. According to the report, decking will remain the leading application, windows and doors will be among the fastest growing types of application.

In recent years, windows, doors, thermal insulating systems, park benches, garden sheds, and sun screens for tower buildings are all made from WPC in China. The concept of using biobased plastics as reinforced matrices for WPC is gaining more and more approval day by day. The developments in emerging biobased plastics are spectacular from a technological point of view and mirror the rapid growth of the market.

The main product in terms of production volumes will be the starch plastics, poly (lactic acid) (PLA), and polyhidroxyalkanoate (PHA).

There is a growing trend to use wood fibres as fillers and/or reinforcers in plastics compared to mineral fillers. Their flexibility during processing, high specific stiffness, and low cost (on a volumetric basis) make wood fibres, attractive to manufacturers. This century has witnessed an ever increasing consumption of plastics as important raw materials, more than 80% of which are thermoplastics as a result of the increased demand.

2.8.1 Building and Construction

WPC industry is a rapidly growing and evolving business. A wide range of entrepreneurial ventures and business development initiatives in larger companies are responsible for the creation of a wide array of new products and the launch of a variety of product lines. WPC products are currently used in or are under development for a wide range of applications in a number of market sectors including the following [13].

The products include cladding (exterior horizontal and vertical), doorframes and their components, ducting, fascias, soffits and barge boards, prefinished floorboards, roofline products, roof tiles , stairs, window frame and their components, and timber.

2.8.2 Interiors/lnternal Finishes

Among interior and internal finish products are balustrades , blinds and shutters, coving, dado rails, decorative profiles , interior panels, kitchen cabinets, laminate flooring, office furniture, shelving, skirting boards , sound proofing, and worktops .

2.8.3 Automotive

The automotive components made from WPCs are mainly restricted in interior parts, such as door and head liners, interior panels, rear shelves, spare tire covers, sound boxes, and truck floors.

2.8.4 Garden/Outdoor

Decking is the leading garden/outdoor application of WPCs . Other outdoor applications include fencing and fence posts, garden furniture, outhouse sheds, park benches, playground equipment, and surfaces.

2.8.5 Industrial

Railings are the most frequent industrial/infrastructure materials application made from WPCs . Handrails, industrial packaging, marine pilings/bulkheads, pallets/crates/totes, piers/docks , rubbish bins , and railway sleepers are the other industrial applications to name a few [23].

2.9 Specialty Composites

Special purpose composite materials are produced to obtain enhanced performance properties like water resistance, mechanical strength, acidity control, and fire, decay and insect resistance. Overlays and veneers can also be added to enhance both structural properties and appearance.

2.9.1 Moisture-Resistant Composites

Sizing agents can be used to make composites resistant to moisture. The common size agents include rosin, wax, and asphalt. Sizing agents cover the surface of fibers, reduce surface energy, and render the fibers relatively hydrophobic. Sizing agents can be applied in two ways. In the first method, water is used as a medium to ensure thorough mixing of sizing and fiber. The sizing is precipitated from the water ad is fixed to the fiber surface. In the second method, the sizing is applied directly to the fibers.

2.9.2 Flame-Retardant Composites

Two general application methods are available for improving the fire performance of composites with fire-retardant chemicals. One method consists of pressure impregnating the wood with waterborne or organic solvent-borne fire-retardant chemicals. The second method consists of applying fire-retardant chemical coatings to the wood surface. The pressure impregnation method is usually more effective and longer lasting; however, this technique is standardized only for plywood. It is not generally used with structural flake/particle/fiber composites as can cause swelling that permanently damages the wood-adhesive bonds in the flake/particle/fiber composite and results in the degradation of some physical and mechanical properties of the composite. For wood in existing constructions, surface application of fire-retardant paints or other finishes offers a possible method to reduce flame spread [24].

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Chapter 3 Lignin

3.1 General properties of lignocellulosic fiber

The three principal components of plant materials are cellulose, lignin, and hemicellulosics (Fig.4).

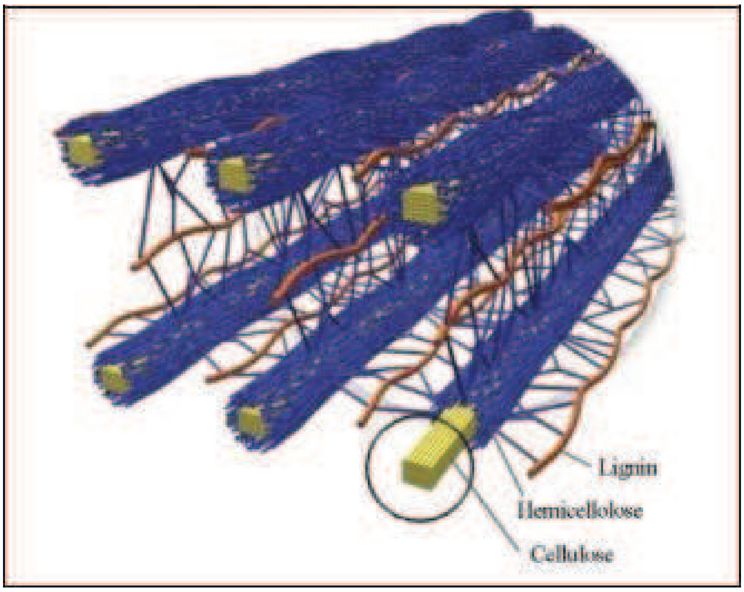


Figure 4-Cellulose strands surrounded by hemicellulose and lignin

Cellulose and hemicellulosics are polysaccharides [1]. Cellulose is a highly regular structure, crystalline polymer, made up of thousands of glucose residues, covalently bound “head-to-tail”(Fig.5):

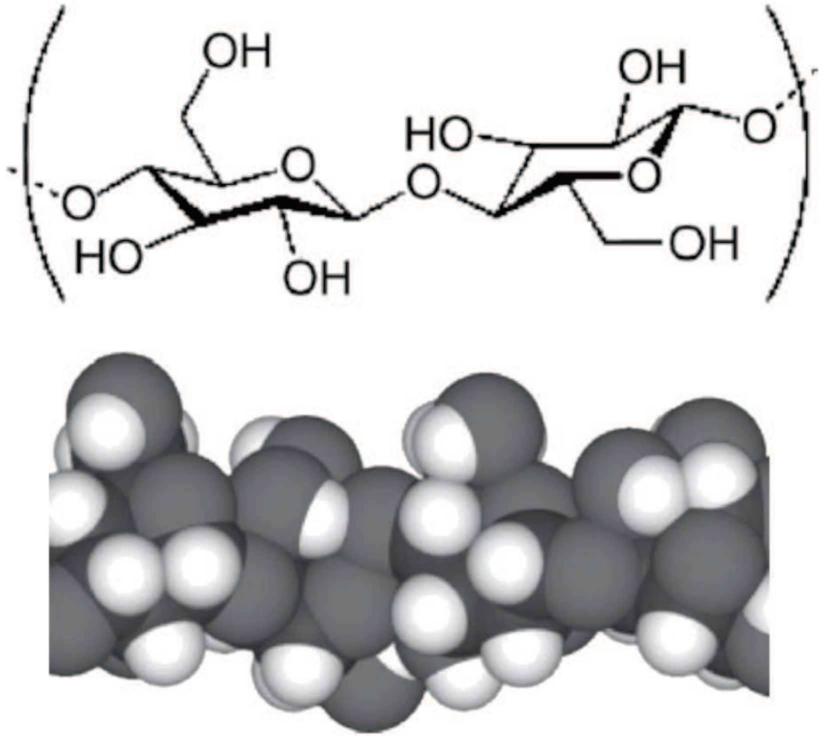


Figure 5- The upper structure shows a block of two glucose molecules in cellulose that is repeated thousands of times to make a more or less complete cellulose chain. Bundles of those chains form a cellulose fiber. The lower structure is a three-dimensional model of the same block of two glucose molecules.

Hemicellulosics form much shorter branched chains consisting of five and six carbon ring sugars. These chains play a role of amorphous soft fillers, wrapping cellulose regions. “Hemicellulosics” is a collective term for a great many structures of heteropolysaccharides of plant origin, forming plant cell walls along with cellulose.

Lignin is a phenol propane-based amorphous solidified resin, filling the spaces between the polysaccharide fibers. Lignin is not just a “concrete” but also a highly engineered chemical structure.

Lignin is a highly polymeric material, crosslinked, highly aromatic structure. Lignin is considered to be largely responsible for strength and durability of wood. In fact, trees stand upright because lignin supports their integrity. Besides, lignin slows down greatly accessibility of wood to cellulolytic microbes. Lignin can be defined as the residue left after the plant material is hydrolyzed with strong acids. Lignin can be considered as one huge polymeric molecule penetrating wood matrix. When one cuts wood, one cuts the single lignin molecule in parts.

Traditionally lignin has been viewed as a waste material or a low value by-product of pulping with its utilisation predominantly limited to use as a fuel to fire the pulping boilers. Indeed it has been estimated that only 1–2% of lignin is isolated from pulping liquors and used for speciality products [1].

This mindset is still with us today in the modern approaches to fuel generation, such as the conversion of biomass into ethanol, where the residual lignin is used as a fuel for power generation to drive the fermentative ethanolification. The time is now ripe to change this view as a result of several factors. Advances in specific chemical processing have meant that the lignins produced either by pulping or other means are no longer necessarily as chemically heterogeneous as they previously were. Also the chemical industries are broadening their end user markets leading to requirements for a feedstock base that can meet the needs of these new end products and imbue them with novel properties. In addition, the increasingly stringent environmental waste regulations, both at the national and European level, mean that all wastes must be dealt with and the diverse chemical moieties inherent in lignins from diverse plant sources and processing/extraction methods mean that it should profit from this via purification, processing and integration into new and established chemical industry subsectors such as polymers, resins, adhesives, etc. The aim here is to show how lignin has or can become integrated into these materials industries and to highlight blossoming lignin research that can use lignin as a novel and appropriate, renewable feedstock rather than as a replacement for synthetic phenolics.

3.2 Lignin structure

Lignin is a complex amorphous polyphenol molecule whose structure and properties basically depends on the raw material, growing conditions of the plant and extraction methods used.

Lignin is primarily a structural material to add strength and rigidity to cell walls and constitutes between 15 wt% and 40 wt% of the dry matter of woody plants. Lignin is more resistant to most forms of biological attack than cellulose and other structural polysaccharides, and plants with a higher lignin content have been reported to be more resistant to direct sunlight and frost [2].

Typical molecular masses of isolated lignin are in the range 1000–20000 g/mol, but the degree of polymerisation in nature is difficult to measure, since lignin is invariably fragmented during extraction and consists of several types of substructures which repeat in an apparently haphazard manner.

The main precursors of lignin are three monomers phenylpropanoids, namely p-coumaryl, coniferyl and sinapyl alcohols (Fig.6) [3].

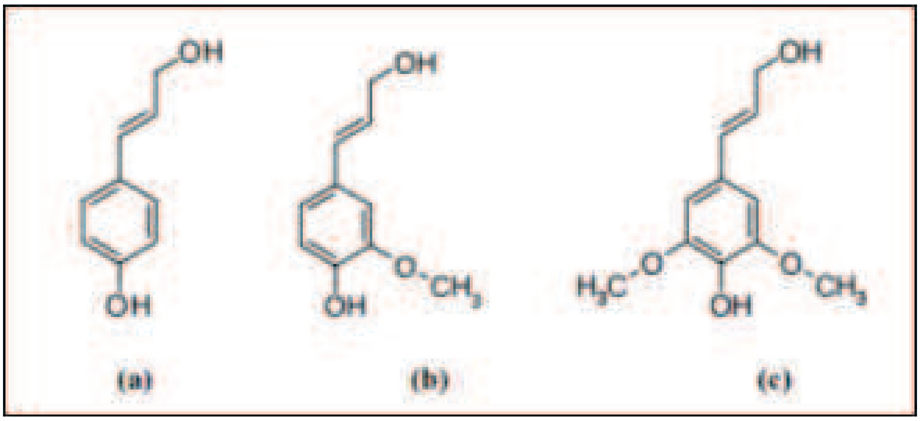
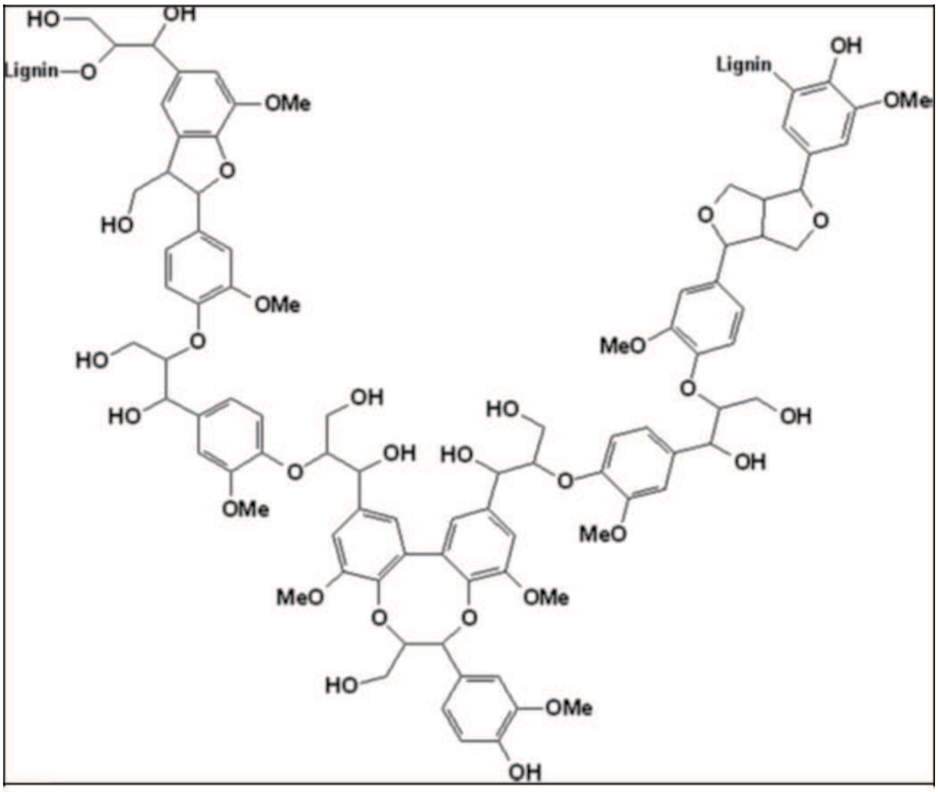


Figure 6-Monolignol monomer species. (a) p-Coumayl alcohol, (b) coniferyl alcohol, (c) sinapyl alcohol

The most common linkages in the lignin molecule are the β-O-4 ether linkages, followed by other types of ether and C-C linkages such as α-O-4, β-5, 5-5, 4-O-5, β-1, and β-β. Although the lignin structure has been intensely studied for many years, the different kinds of linkages in lignin and their diversity of functional groups, like methoxyl groups, phenolic and aliphatic hydroxyl groups principally, result in a complicated macromolecule (Fig.7) [4].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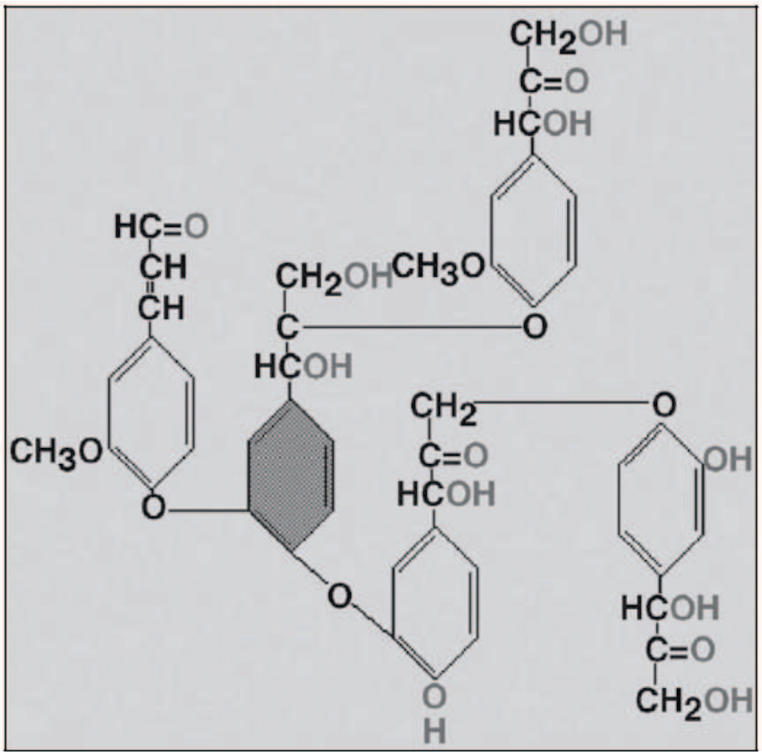
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C=O
CH2OH

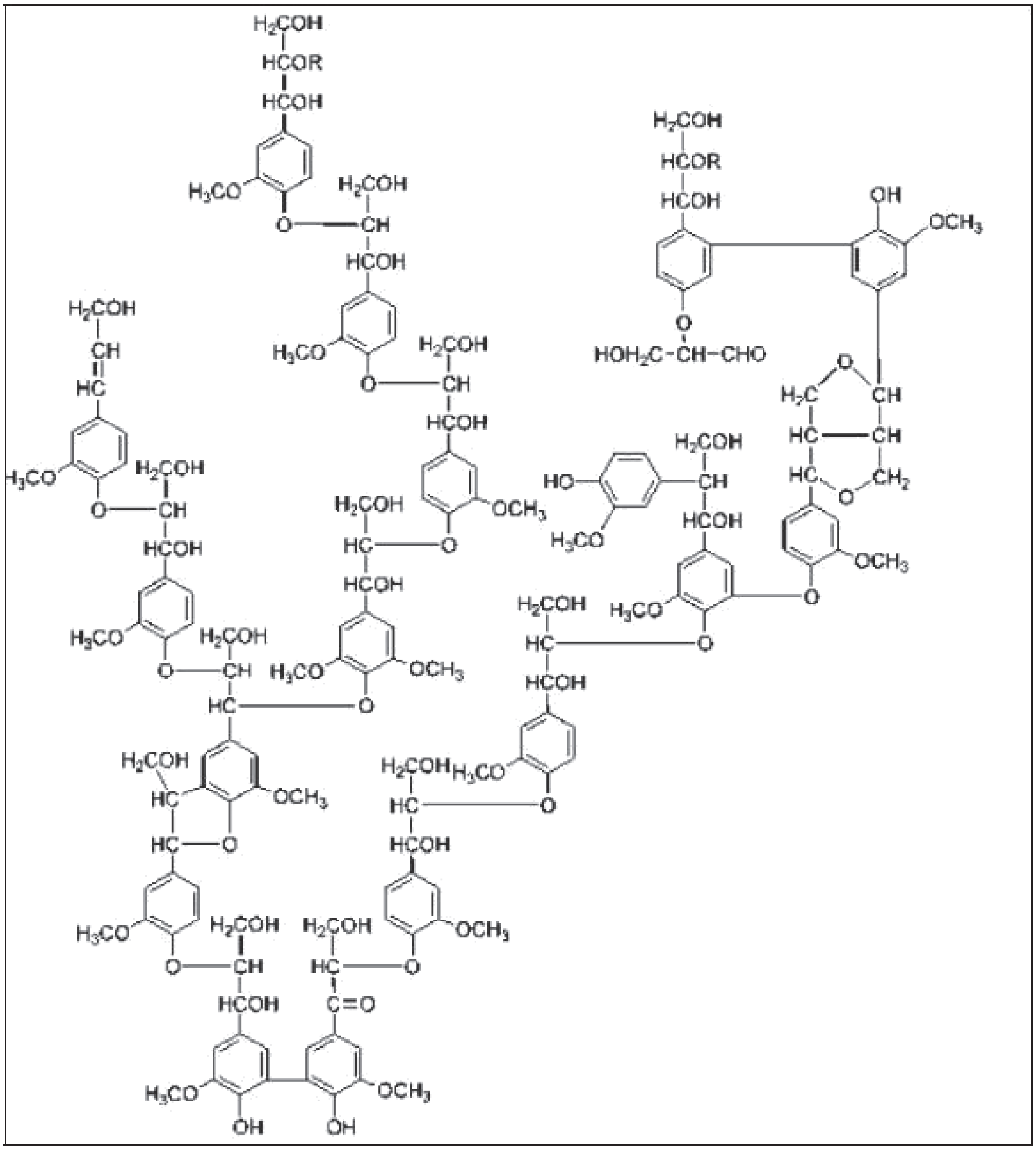

Figure 7- Several possible presentations of structures of lignin

3.3 Physical properties of lignin

The physicochemical state of lignin dictates how and where it can be utilised in the manufacture of various products. The source from which lignin is obtained and the method of extraction has a strong bearing on its properties. As a highly crosslinked material with widely varying functionality, lignin may not readily be characterised to give meaningful molecular weight data, but other parameters more directly relevant to end-use properties may be assessed. Despite this, the molecular weight data does provide some useful guide.

Table 1 gives the functional groups and molecular weight of selected lignins. The reactivities of these lignins will impact on the attributes of the end products.

Table 1 - Molecular weight and functional groups of lignins [5]

Lignin type	**M_n (g/mol)**	**COOH (%)**	**OH phenolic (%)**	**Methoxy (%)**
Soda (bagasse)	2160	13,6	5,1	10
Organosolv (bagasse)	2000	7,7	3,4	15,1
Soda (wheat straw)	1700	7,2	2,6	16
Organosolv (Hardwood)	800	3,6	3,7	19
Kraft (Softwood)	3000	4,1	2,6	14

For example, kraft lignin-based phenol formaldehyde resins have superior properties to steam exploded lignin-based phenol formaldehyde resins.

Another important parameter is the glass transition temperature, T_g, which is an indirect measure of crystallinity and degree of crosslinking and directly indicates the rubbery region of the material (Table 2).

Table 2 - T_g of different lignin types [6]

Types of lignin	**T_g (°C)**
Hardwood	110-130
Softwood	138-160
Kraft Lignin	124-174
Orgonosolv lignin	91-97
Steam explosion lignin	113-139

Lignin T_g will depend on the amount of water and polysaccharides, as well as molecular weight and chemical functionalisation, but in general the T_g will be lower the greater the mobility of the lignin molecules.

The reactivity and physicochemical properties of lignins are dependent to certain extent, on their molecular weight distribution. More potential applications of lignin can be realised if the miscibility of lignin with other polymeric materials can be improved. This may be done through chemical modification of lignin with appropriate hydrophobic groups (e.g., butyrate, hydroxypropyl, ethyl) or through formation of lignin copolymers [7].

3.4 Lignin fractionation processes

The extraction of lignin from lignocellulosic materials is conducted under conditions where lignin is progressively broken down to lower molecular weight fragments, resulting in changes to its physicochemical properties. Thus, apart from the source of the lignin, the method of extraction will have a significant influence on composition and properties of lignin. The majority of lignin extraction and delignification processes occur by either acid or base-catalysed mechanisms.

3.4.1 Sulfite process

At present the main commercial source of lignin is from the pulp and paper industry. The sulfite process which traditionally used to be the main pulping technology involves the reaction of a metal sulfite and sulfur dioxide.

The main reactions that take place during the pulping process are: (a) the reaction between lignin and free sulphurous acid to form lignosulfonic acid, (b) the formation of the relatively soluble lignosulfonates with the cations, Mg, Na or NH_4^+, and (c) the fragmentation of the lignosulfonates.

In addition to lignosulfonates, degraded carbohydrates are also produced. The pulping reactions are usually conducted between

140 °C and 160 °C and the pH of the acid sulfite process is between 1.5 and 2.0, while the bisulfite process is between pH 4.0 and 5.0. Several purification steps are required to obtain the lignosulfonate fraction with high purity, including fermentation to convert the residual sugars to ethanol and membrane filtration to reduce the metal ion content. The lignosulfonate biopolymer is typically highly crosslinked, with ~5 wt% sulfur content, and bears two types of ionizing groups; sulfonates ($pK_a \leq 2$) and phenolic hydroxy groups (pK_a ~10). Because of the low pK_a for the sulfonate groups, lignosulfonates are water-soluble under most conditions.

The physicochemical properties of lignosulfonates are affected by the metal cation (Na or Ca) of the sulfite salt used during the pulping process. Sodium sulfite produces more extended lignin chains that are more suitable for use as dispersants, while calcium sulfite produces more compact lignin, presumably due to a bridging effect of chelating Ca^{2+}. The sulfur content (5 wt%) of sulfite lignins is one of the major factors restricting its use in speciality applications, and so most of its lignin is currently used for energy generation.

The sulfite delignification process is an acid catalysed process in which there is cleavage of the α-ether linkages and β-ether linkages of lignin. The process goes via the quinone methide intermediate or nucleophilic substitution. Generally, less side-chain cleavage is seen under acid-catalysed rather than alkali-catalysed reactions.

The complete breakdown of the aryl ether linkages leads to the formation of a reactive resonance-stabilised benzyl carbocation. Under these conditions condensation reactions occur. The carbocation may form a C–C bond with an electron-rich carbon atom in the aromatic ring of an lignin fragment or the protonation of a benzylic oxygen atom may cause inter- or intramolecular condensation by a SN_2 mechanism. The formation of organic acids such as acetic acid during the delignification process can encourage the formation of the benzylic carbocation or lead to protonation of a benzylic oxygen atom, enhancing the SN_2 condensation pathway [8].

3.4.2 Kraft process

The kraft or sulfate process is now the main traditional method for pulping and hence produces the largest volume of lignin. It uses sodium hydroxide and sodium sulphide under strong alkaline conditions to cleave the ether bonds in lignin.

The delignification process proceeds in three stages. The first phase occurs around 150 °C and is controlled by diffusion. The second stage occurs between 150 °C and 170 °C, while the final stage occurs at even higher temperatures. The bulk of the delignification (90 wt%) occurs during the second stage. The lignin may be recovered from the alkaline liquid remaining after pulp extraction, the black liquor, by lowering the pH to between 5 and 7.5 with acid (usually, sulfuric acid) or carbon dioxide.

The kraft process produces lignin with aliphatic thiol groups called kraft lignin. Kraft lignin is hydrophobic and so needs to be modified to improve reactivity. The high sulfur content (1–2 wt%) of kraft

lignin is also a major reason why its main application has been in energy generation in pulp mills.

The kraft process goes by alkaline hydrolysis in which the β-1,4 links in cellulose is cleaved, allowing the lignin component of biomass to be extracted. However, the lignin itself is also susceptible to attack by alkali and except for the diarylether linkages, ethers in lignin readily undergo base-induced hydrolysis under relatively mild conditions.

In alkaline hydrolysis α-aryl ether bonds are more easily broken than β-aryl ether bonds, particularly in situations where the substructures contain a free phenolic hydroxyl group in the para position.

Simple heating of the biomass in water results in substantial cleavage of the α-ether bonds either through a quinone methide intermediate or through nucleophilic substitution by a SN_2 mechanism.

In alkaline media intermolecular condensation reactions can occur with competition between the added nucleophiles and anionic lignin fragments (e.g., phenolate anions and carbanions). The extent of condensation will depend on the types of structures initially formed. If a structure contains good leaving groups at the β-carbon, neighboring group participation reactions resulting in the cleavage of β-aryl ether linkages will predominate over condensation reactions.

3.4.3 Soda process

The soda process (which goes by alkaline hydrolysis) was the first chemical pulping method and was patented in 1845. Soda process led kraft pulping which now dominates the chemical pulping industry. The soda process is now becoming the predominant method for chemical pulping of non-wood material such as bagasse, wheat straw, hemp, kenaf and sisal. This is mainly due to the development of both low cost chemical recovery methods and effective effluent treatment technology. It may also be due to less stringent environmental legislation for effluent discharge in some countries.

The pulping process involves heating the biomass in a pressurized reactor to 140–170 °C in the presence of 13–16 wt% alkali (typically sodium hydroxide).

Lignin recovered through extraction with sodium hydroxide is normally referred to as ‘soda lignin’. Soda lignin from non-wood sources is typically difficult to recover by filtration or centrifugation because its high carboxylic acid content, arising from oxidation of aliphatic hydroxy groups, makes it a relatively good dispersant.

Heating is therefore required to encourage coagulation and ensure filtrable material can be obtained.

As soda lignin contains no sulfur and little hemicellulose or oxidised defect structures, it has good potential for use in high value product [9].

3.5 Lignin as a base material for materials applications

There are many commercial applications of low value where lignins (predominantly lignosulfonates) are used because of their surface-active properties.

Due to the enormity of the task, the study of lignin in materials applications will be subdivided into specific subsectors although there is some overlap between these: phenolic resins, epoxies, adhesives, polyolefins and miscellaneous.

Lignin should be an obvious candidate for application as a phenol substitute in phenol formaldehyde resins but its chemical heterogeneity is the limiting factor and, at an additive level of 5–10% of the resin weight, has led to the production of resins with increased M_W. This can be countered however via several avenues:

- *(Bio)chemical modification of the lignin.*

Reaction with enzyme systems to oxidatively crosslink the lignin or pre-reaction of the lignin with methylolated phenols increased its reactivity.

- *The addition of filler agents.*
- *Employing novel process derived lignins.*

The use of lignin in this resin field is one of adjunct crosslinker within the normal classic epichlorohydrin reaction wherein lignin would impart the bulk properties. For these applications the lignin must be impurity free, i.e. free of salts, water and sugars. This can be achieved by purifying waste lignins (precipitation, deionisation, etc.) derived from the common pulp and paper processes (Kraft, Soda, etc.) or direct use of lignin from the less condensing pulping processes such as Alcell, non-wood fibres pulping.

3.5.1 Protein–lignin blends

Proteins have long been used for the production of plastics and resins. The main drawbacks of protein-based materials are high water absorption and the difficulty of separating the proteins from naturally occurring colourants without denaturation, but these obstacles are gradually being overcome. As a crosslinked material with a largely aromatic structure, lignin has the capacity to increase the tensile strength, Young's modulus, thermal stability and elongation at break of protein materials.

Thermoplastic materials comprising lignin and protein blended with natural rubber have been shown to have improved impact resistance compared to lignin-free formulations.

Hydrogen-bonding interactions are often insufficient to ensure adequate mixing of lignin with protein.

An alternative strategy for enhancing the compatibility of lignin with protein, rather than adding a compatibiliser, is chemical or enzymatic modifications of the lignin [10].

3.5.2 Starch–lignin blends

The use of starch-based films for packaging materials has increased recently as they degrade readily in the environment in comparison to conventional synthetic materials. However, a significant disadvantage of starch films is that they have very poor water resistance. Blending with hydrophobic polymers can clearly improve the water resistance of starch, and lignin has a high compatibility with starch making it an obvious candidate for blending.

These blends gave significant improvements in water resistance. The higher water resistance of lignin/starch blends is attributable to the partial compatibility of lignin with the amylose component of starch, the presence of hydrophobic lignin at the surface of the material due to surface activity of phenolic groups, and crosslinking between the starch-rich phase and the lignin-rich phase.

3.5.3 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHA) are a group of biodegradable and biocompatible linear aliphatic polyesters mainly composed of R-(−)-3 hydroxyalkanoate units, produced as carbon and energy storage materials by a range of algae and bacteria. Unlike most biopolymers, PHA are insoluble in water and have low permeability towards oxygen, carbon dioxide and water. These barrier properties make PHA good candidates for the production of packaging products like bottles, bags, wrapping film and disposable nappies. These applications have not been fully realised because PHA is relatively stiff and brittle and are thermally unstable during processing.

Blending with lignin is one possible strategy for overcoming the mechanical disadvantages of PHA [11].

3.5.4 Epoxy resin blends

Substitution of lignin for phenol is a possible route toward the preparation of inexpensive and renewable epoxy-resin adhesives.

The effect of lignin blending with epoxy resins is strongly affected by the type of lignin used [12].

3.5.5 Lignin–polyolefin and Rubber–lignin blends

The main objectives of incorporating lignin in polyolefins are to act as a stabiliser against oxidation under UV radiation or at elevated temperatures, or conversely, to enable the biodegradation of the material.

Lignin has attracted most attention as filler in natural and synthetic rubbers that is, as a component of a multiphase mixture, not in a homogeneous blend [13].

3.5.6 Polylactides and polyglycolides

Poly(L-lactic acid) (PLA) is a crystalline biodegradable polymer which like PHA has poor processing properties because of its high crystallinity. Copolymers of L-lactic acid and L-glycolic acid are frequently used in biomedical applications to enable tailoring of flexibility and degradation rate [14].

The results of the thermal and mechanical properties of PLA/lignin blends, indicate a strong intermolecular hydrogen-bonding interaction between PLA and lignin. The tensile strength and elongation at break decreased with lignin content, while the Young’s modulus remained almost constant up to a lignin content of 20 wt%. At lignin content greater than 20 wt%, thermal degradation of PLA was enhanced. More recently, ring-opening polymerisation of cyclic lactides with lignin has been used to create graft-copolymer additives that can significantly reduce the crystallinity and improve the processing and end-use performance of PLA.

Lignin has also been added to PLA in order to reduce its flammability, giving performance competitive with commercial intumescent formulations [15].

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Chapter 4 Recycling of bioplastics, blends and biocomposites

Sustainable use of carbon sources, regardless of whether they are bio-based or fossil, must involve production of recyclable plastics. Both petro- and bio-based plastics will coexist in the production of sustainable and cost-effective materials for a long time to come. Thus, the increased use of bioplastics and biocomposites may have serious implications for the recycled plastics industry in the near future. Where it is cost effective to recycle, conventional plastics recycling operations are already well established and driven by industry. However, the introduction of 'green' plastics to the market has created a number of issues that need to be addressed. One important question concerns the potential risk of contamination of the collected conventional plastics. In addition, there are concerns about the cost of separation, and about increased contamination, yield loss and impact on recycled materials quality and processing. Another important issue is to develop technologically viable, effective, efficient and economical recovery systems and end markets for post-consumer bio-based materials without jeopardizing the existing recycling systems [1].

Sustainable bio-based eco-products are products with commercial and environmental acceptability that are derived from renewable resources, and have recycling capabilities and/or triggered biodegradability [2]. As a result of new legislation on the development of environmentally and economically viable manufacturing as well as reuse and recycling of materials, the market for biopolymers and biocomposites is growing rapidly [3].

The term bioplastic means a plastic produced from a biological source (short carbon cycle) while the term biodegradable refers to a material that can be degraded relatively rapidly by microbes in a bio-active environment under suitable conditions. All (bio- and petroleum-based) plastics are theoretically biodegradable; however, most materials degrade at such slow rates that they are considered non-biodegradable or durable. Biodegradable plastics were introduced in the 1980s to find ways to produce non-petroleum-based plastics, as well as to reduce the environmental effects because of the increased landfill [4]. Biodegradable plastics have dominated the bioplastics market with a roughly 90% share. However, durable plastics based on renewable resources are forecasted to increase their market. One important reason is legislation. The directive has already encouraged development of partly bio-based resins, alloys or blends of bio- and petrochemical-based materials (called hybrid bioplastics). Most durable bioplastics are being blended today with petrochemical-based polymers such as polycarbonate (PC), polypropylene (PP), acrylonitrile– butadiene–styrene (ABS), high-impact polystyrene (HIPS), poly(ethylene terephthalate) (PET) and poly(methyl methacrylate) (PMMA). Bio-based and biodegradable polymers have a wide range of applications, such as in the biomedical, packaging and agricultural fields. The most common of the biodegradable materials are blends of thermoplastic starch (TPS) and aliphatic/aromatic polyesters, such as poly(lactic acid) or polylactides (PLA), polycaprolactone (PCL), poly(butylene adipate terephthalate) (PBAT) and poly- hydroxybutyrate (PHB) [5].

4.1 Poly(lactic acid), PLA

PLA is a thermoplastic aliphatic polyester obtained from the ring-opening polymerisation of lactide, which may be derived from the fermentation of sugar feedstock at competitive prices [6].

4.1.1 PLA Production

There are several industrial routes to usable (i.e. high molecular weight) PLA. Two main monomers are used: lactic acid, and the cyclic di-ester, lactide.

The most common route to PLA is the ring-opening polymerization of lactide with various metal catalysts in solution, in the melt, or as a suspension. The metal-catalyzed reaction tends to cause racemization of the PLA, reducing its stereoregularity compared to the starting material. Another route to PLA is the direct condensation of lactic acid monomers. This process needs to be carried out at less than 200°C; above that temperature, the entropically favored lactide monomer is generated. This reaction generates one equivalent of water for every condensation (esterification) step, and that is undesirable because water causes chain-transfer leading to low molecular weight material. The direct condensation is thus performed in a stepwise fashion, where lactic acid is first oligomerized to PLA oligomers [7]. Thereafter, polycondensation is done in the melt or as a solution, where short oligomeric units are combined to give a high molecular weight polymer strand. Water removal by application of a vacuum or by azeotropic distillation is crucial to favor polycondensation over transesterification. Molecular weights of 130 kDa can be obtained this way. Even higher molecular weights can be attained by carefully crystallizing the crude polymer from the melt. Carboxylic acid and alcohol end groups are thus concentrated in the amorphous region of the solid polymer, and so they can react. Molecular weights of 128–152 kDa are obtainable thus [8].

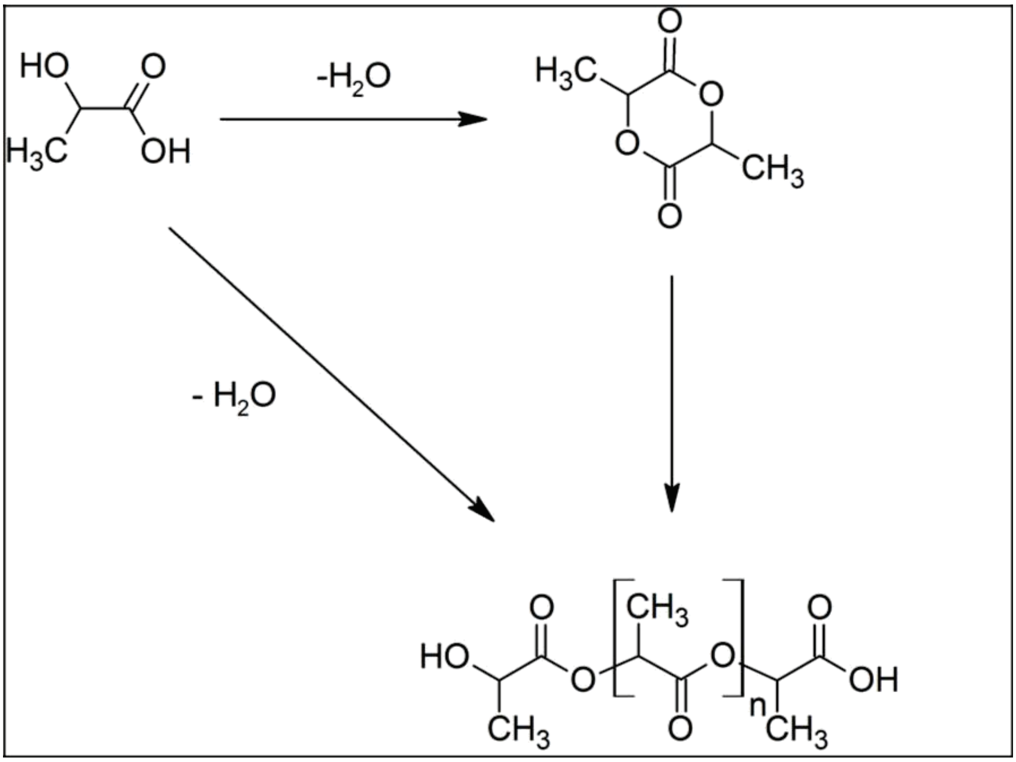


Figure 8- PLA polymerization[9]

Polymerization of a racemic mixture of L- and D-lactides usually leads to the synthesis of poly-DL-lactide (**PDLLA**), which is amorphous (Fig.8). Use of stereospecific catalysts can lead to heterotactic PLA which has been found to show crystallinity. The degree of crystallinity, and hence many important properties, is largely controlled by the ratio of D to L enantiomers used, and to a lesser extent on the type of catalyst used. Apart from lactic acid and lactide, lactic acid *O*-carboxyanhydride, a five-membered cyclic compound has been used academically as well. This compound is more reactive than lactide, because its polymerization is driven by the loss of one equivalent of carbon dioxide per equivalent of lactic acid. Water is not a co-product [10].

4.1.2 Chemical and physical properties

Due to the chiral nature of lactic acid, several distinct forms of polylactide exist: poly-L-lactide (**PLLA**) is the product resulting from polymerization of L,L-lactide (also known as L-lactide). PLLA has a crystallinity of around 37%, a glass transition temperature 60–65 °C, a melting temperature 173–178 °C and a tensile modulus 2.7–16 GPa. Heat-resistant PLA can withstand temperatures of 110°C. PLA is soluble in chlorinated solvents, hot benzene, tetrahydrofuran, and dioxane.

Polylactic acid can be processed like most thermoplastics into fiber (for example, using conventional melt spinning processes) and film. The melting temperature of PLLA can be increased by 40–50 °C and its heat deflection temperature can be increased from approximately 60 °C to up to 190 °C by physically blending the polymer with PDLA (poly-D-lactide). PDLA and PLLA form a highly regular stereocomplex with increased crystallinity (Fig.9) [11].

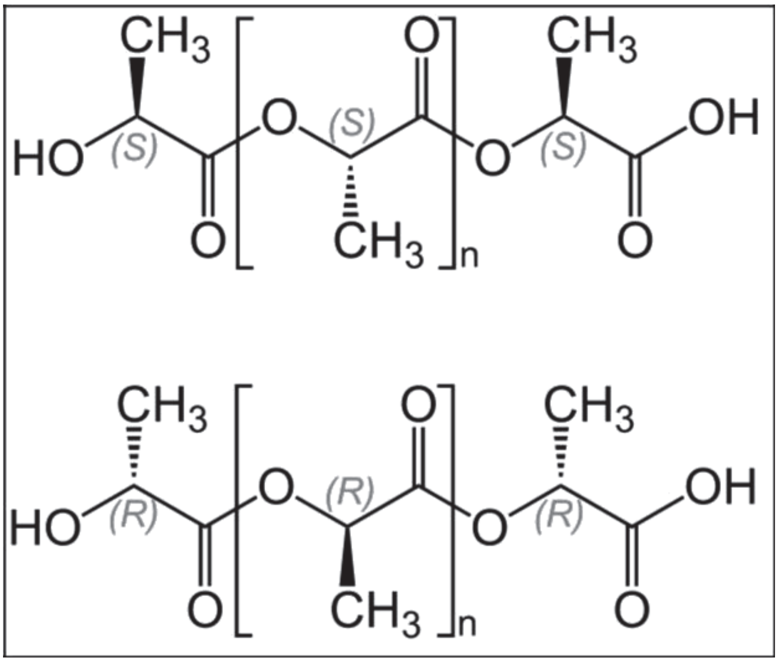


Figure 9- PLA Stereoisomers [12]

The temperature stability is maximised when a 1:1 blend is used, but even at lower concentrations of 3–10% of PDLA, there is still a substantial improvement. In the latter case, PDLA acts as a nucleating agent, thereby increasing the crystallization rate. Biodegradation of PDLA is slower than for PLA due to the higher crystallinity of PDLA.

4.1.3 Uses

PLA can be processed by extrusion, injection molding, film and sheet casting, 3D printing, and spinning, providing access to a wide range of materials.

Being able to degrade into innocuous lactic acid, PLA is used as medical implants in the form of anchors, screws, plates, pins, rods, and as a mesh. Depending on the exact type used, it breaks down inside the body within 6 months to 2 years. This gradual degradation is desirable for a support structure, because it gradually transfers the load to the body (e.g. the bone) as that area heals.

PLA can also be used as a decomposable packaging material, either cast, injection-molded, or spun.

Cups and bags have been made from this material. In the form of a film, it shrinks upon heating, allowing it to be used in shrink tunnels. It is useful for producing loose-fill packaging, compost bags, food packaging, and disposable tableware. In the form of fibers and non-woven textiles, PLA also has many potential uses, for example as upholstery, disposable garments, awnings, feminine hygiene products, and diapers (Fig.10) [13].

Racemic and regular PLLA has a low glass transition temperature, which is undesirable. A stereocomplex of PDLA and PLLA has a higher glass transition temperatures, lending it more mechanical strength. It has a wide range of applications, such as woven shirts (ironability), microwavable trays, hot-fill applications and even engineering plastics (in this case, the stereocomplex is blended with a rubber-like polymer such as ABS). Such blends also have good form stability and visual transparency, making them useful for low-end packaging applications

PLA is also used as a feedstock material in 3D printers. The properties enable PLA printed solids to be encased in plaster-like moulding materials, then burned out in a furnace, so that the resulting void can be filled with molten metal.

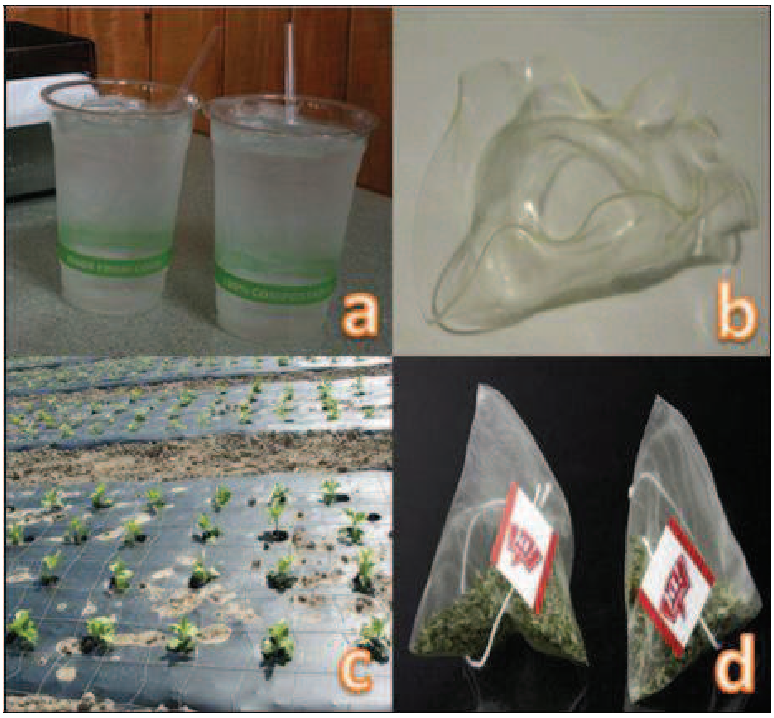


Figure 10- 3Some uses of PLA (a)Biodegradable PLA cups in use at a restaurant (b)Due to PLA's relatively low glass transition temperature, PLA cups cannot hold hot liquids (c) Mulch film made of PLA-blend "bio-flex" (d) Tea bags *made of PLA[53]*

PLA, which benefits both from coming from renewable resources and being biodegradable in the compost environment, has attracted much attention. It has become an economically viable commodity plastic in industry and is employed to produce common-use articles and packaging materials such as trays, bottles or films for the food packaging industry. This polymer has good mechanical properties and processability and good thermal properties, but also has limited environmental impact according to life cycle assessment (LCA).

PLA, like most thermoplastics, can be moulded into bottles, containers and so on by injection moulding, blow moulding, etc., or be extruded into fibres, films and sheets.

Natural bio-fibre composites are emerging as a viable alternative to glass-fibre reinforced plastics, especially in automotive applications [14].

Thermoplastic biocomposites, composed of PP, PE, PS or biopolymers such as PLA and reinforced with natural fibres have especially attracted great attention during the past few years. Such thermoplastic biocomposites, compared with those made using a thermoset matrix, can be processed into different shapes and have the potential to be mechanically recycled. Biocomposites, composed of natural fibres and bio-resins, have also been introduced into the market because of the increasing demand for advantageous mechanical properties per weight, important for environmental adaptation of products as well as improving product performance. Biocomposites with a biopolymer matrix are the future of 'green composites' and their recycling makes it possible to retain the whole carbon content and save primary resources; furthermore, they offer reductions in weight and cost, and give less reliance on foreign oil resources. Biocomposites are currently used mainly in the automotive, construction, furniture and packaging industries, where renewable products are attracting great attention because of the driving force of increasing environmental awareness and depletion of fossil resources.

The key measurement tool to assess a product's environmental impact is LCA. Through LCA it is possible to account for all of the environmental impacts associated with a product, covering all stages in a product's life, from the extraction of resources to waste disposal. However, using renewable feedstock does not guarantee that a plastic is environmentally friendly over its entire life cycle. The sustainability benefits of using renewable feedstock may not be sufficient if the material cannot be recycled. To study the recyclability of the polymeric materials including bio-plastics and their derivatives, it is a well-tried practice to simulate the mechanical recycling by doing multiple extrusions and to find the durability or service life by accelerated thermal and hydrothermal ageing. These methods make it possible to assess the effects of thermal, hydrothermal and thermomechanical degradation [15].

4.2 Mechanical recycling of neat PLA

PLA is one of the most studied bioplastics regarding recyclability. PLA can biodegrade under certain conditions, such as the presence of oxygen and moisture [16]. Although

PLA is biodegradable, which significantly reduces the negative environmental impact of PLA waste, the material recycling and investigation of changes in the properties of PLA upon its multiple processing are important. The first reason for this is that the generation of industrial waste is inevitable in various industrial processes where an online grinding of the offcuts and blending with neat polymer is integrated; the second reason is the possibility to reuse the post-production (used) PLA waste because it would be advisable to extend their service lives before finally discarding them to bio-disposal facilities such as composting plants. Finally, the low environmental impact of PLA would be compromised if the recycling of industrial wastes cannot be achieved [17-19].

Multiple extrusion of PLA up to 10 times was investigated using a double-screw extruder for granulation of PLA followed by laboratory injection moulding press, for preparation of the test samples. The tensile strength values of PLA did not significantly depend on the number of extrusion cycles and they were a little different from each other, showing a slight total reduction of ca. 5.2% after 10 extrusion processes (Fig. 11)
[20].

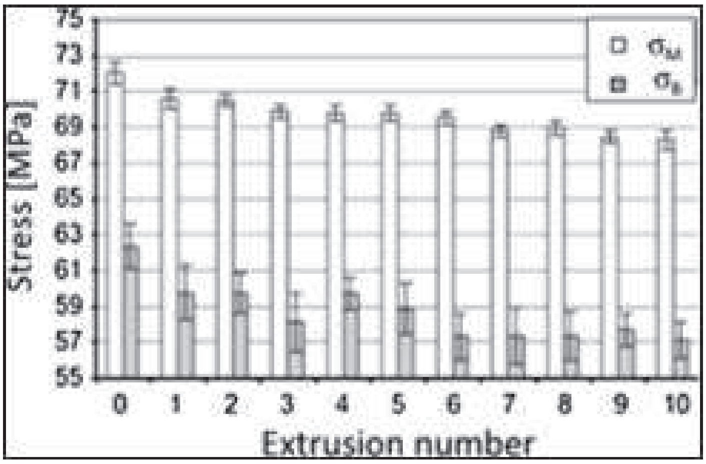


Figure 11- Tensile strength (σ_M) and tensile stress at break (σ_B) as functions of the extrusion number

The decrease in tensile strain was also small (2.2–2.4%) and did not depend on the extrusion number.

The impact strength clearly decreased with raising the number of extrusions (20.2% after 10 extrusion processes).

The thermal characteristics showed a slight decrease of thermal stability of PLA, lowered cold crystallization temperature and a slight reduction of the melting point with increasing number of cycles, and no effect on the glass transition temperature.

The viscosity of PLA decreases greatly (from 3960 to 713 Pa*s) after only one injection cycle. Zero viscosity (η_0) of PLA as a function of injection number is presented in Fig. 12 [21].

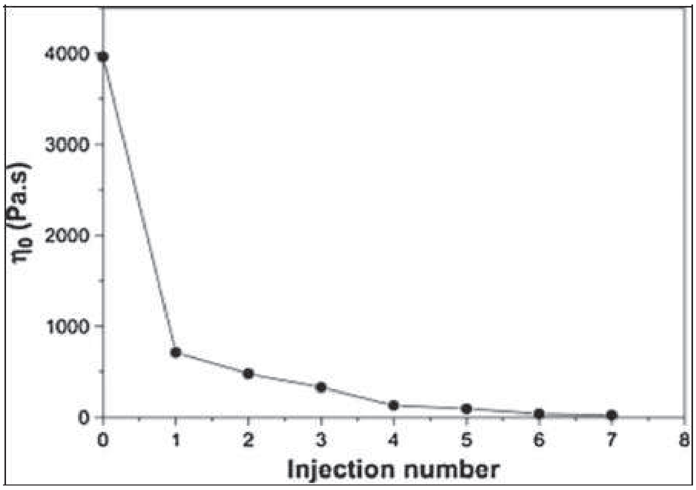


Figure 12- Zero viscosity of PLA as a function of injection number

The mechanical properties of the recycled PLA had become too poor for an industrial application of the polymer.

This dramatic effect of repeated processing cycles was mainly attributed to degradation of PLA by chain scission during processing, which yields a significant decrease in the molecular weight.

To understand the degradation phenomena in PLA, two stabilizers, quinone (PLA-Q) and tropolone (PLA-T) were blended with PLA. Quinone was found to be an efficient stabilizer that traps free radicals and maintains PLA chain length at the processing temperatures. This confirms that the main mechanism of the degradation of PLA is through formation of free radicals and not by the hydrolysis caused by moisture. During the multiple mechanical recycling of amorphous

PLA (95.75 mol% of L-lactic acid and 4.25 mol% of D-lactic acid), chain scission occurs as a result of thermomechanical degradation because, although PLA remained amorphous throughout the reprocessing cycles, a cold-crystallization during differential scanning calorimetry (DSC) and DMTA measurements occurred, with the enthalpy (h_{CC}) increasing with each reprocessing step [22].

DSC data of virgin PLA (VPLA) and of reprocessed PLA (RPLA) are presented in Table 3.

Table 3 - Evolution parameter in VPLA and RPLA

Material	T_g *(°C)*	T_{CCO} *(°C)*	T_{CC} *(°C)*	h_{CC} *(Jg^{-1})*	h_M *(Jg^{-1})*
VPLA	57.2±0.1	106.2±1.7	123.5±0.2	2.21±1.7	2.19±0.04
RPLA-1	56.7±0.1	105.6±0.3	117.3±0.3	23.37±1.7	23.83±0.67
RPLA-2	56.5±0.1	102.0±0.1	110.2±0.4	28.52±1.7	29.77±1.70
RPLA-3	56.7±0.1	101.2±0.6	109.1±1.0	28.32±1.7	27.33±0.97
RPLA-4	56.8±0.1	100.1±0.3	107.3±0.5	27.41±1.7	26.94±0.52
RPLA-5	56.6±0.1	99.6±0.2	106.4±0.1	28.53±1.7	28.31±1.04

(T_G : glass temperature, T_{CCO} and T_{CC} : cold-crystallization in DSC characterized by induction and peak temperatures respectively, Δh_{CC} : cold-crystallization enthalpy, Δh_M : specific melting enthalpy) [23].

Fig. 13 represents the mass-loss profiles of VPLA and of RPLA reprocessed five times (RPLA-5), simuling the thermal behaviour of virgin and multiple-injected PLA facing combustion, using multi-rate linear non-isothermal thermogravimetric experiments under oxygen.

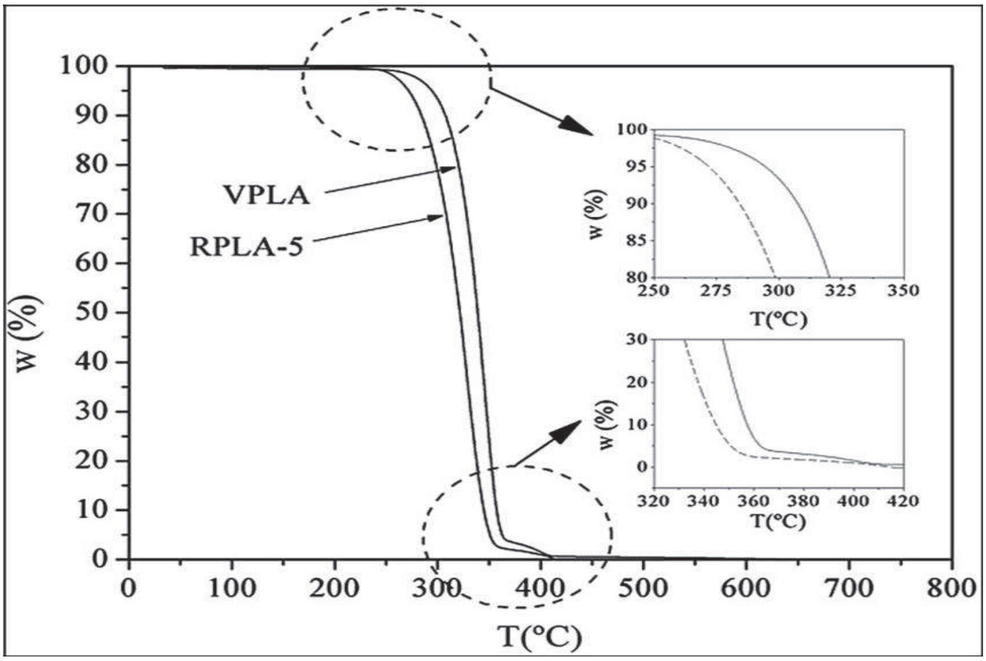


Figure 13-Mass-loss profiles of virgin PLA and PLA reprocessed five time [24].

The water diffusion rate decreased with increasing number of reprocessing cycles, and increased with higher hygrothermal ageing temperatures. The degradation was confirmed to be due to the chain scission reactions promoted by temperature; however, with the presence of water in the polymer matrices, hydrolytic chain scission also occurred, which was especially noticeable for reprocessed PLA and higher temperatures. The effects of hygrothermal ageing were particularly significant at higher temperatures and for PLA reprocessed more than once.

The features of processed PLA strongly depend on its stereochemistry and the impact of the proportion of L- and D-enantiomers. Low amounts of the D-enantiomer (below 1.5 wt%) can accelerate the crystallization process; spherulite growth speed depends on molecular weight and increases upon decreasing the molecular weight. A remarkable level of brittleness has been observed, especially after processing via injection moulding. The proportion of L- and D-enantiomers can affect the possibility of the presence of a crystalline phase after a certain number of processing cycles that might affect the performance of PLA because of decoupling of amorphous and crystalline phases, decreasing chain mobility and modification of the mechanical properties with further processing. PLLA is semi-crystalline and shows a high mechanical strength, whereas PLA (poly(D,L-lactic acid)) is essentially amorphous, or has a low crystallinity, because of its intrinsic structure [25].

4.3 Mechanical recycling of other neat biopolyesters

Polyhydroxyalkanoates (PHAs) have useful mechanical properties and excellent biodegradability. However, they are still expensive and polyhydroxybutyrate (PHB) in particular is quite brittle. PHAs can be mechanically recycled with some loss of molecular weight and mechanical properties.

Recently, a bioplastic copolymer, polyhydroxybutyrate-co-valerate (PHBV), has been mechanically recycled, showing that PHBV is recyclable for up to five cycles, because the reprocessing cycles did not significantly affect the mechanical properties (tensile testing, flexural testing and impact toughness). After reprocessing, the mechanical properties (tensile, flexural and impact strength) were maintained for four cycles; however, they showed a slight decrease after the fifth cycle (7.1%) [26].

4.4 Chemical and biological recycling of neat bioplastics

Although mechanical recycling of plastics is the most favourable technology for the industry, it still has some limitations. It may be difficult to convert PLA waste into useful products considering the previously mentioned reprocessing behavior of PLA, especially thermomechanical degradation during extrusion. Therefore, after each cycle the product quality is lower compared with the starting material and thus its market value decreases. On the other hand, maintaining the quality of the recyclate is vital for ensuring the feasibility of the process and the market value [27].

In chemical recycling, the polymer chain molecules are broken down into smaller hydrocarbon molecules (e.g., monomers), which are then fed into the polymerisation process.

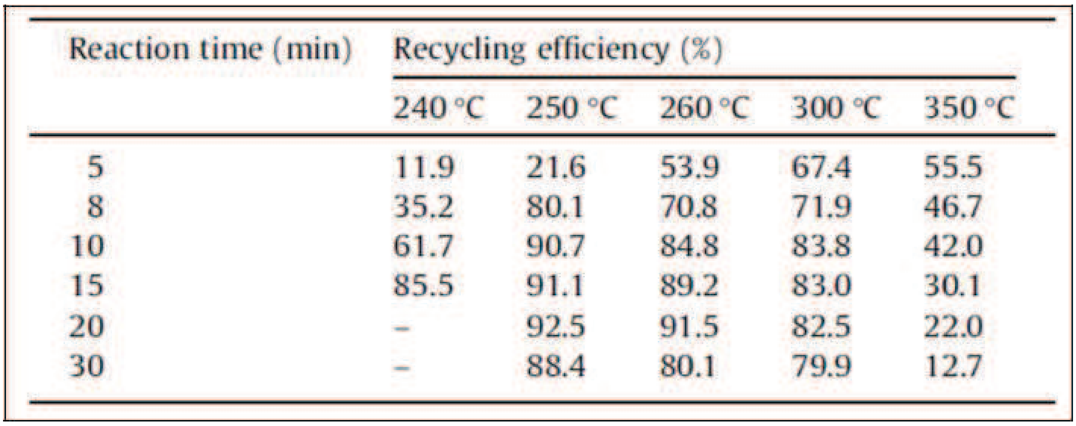
Two main processes have been used for chemical recycling of PLA. The first one is hydrolysis of PLA at high temperatures to obtain lactic acid, and the second one is thermal degradation of PLA to prepare L,L-lactide, which is a cyclic dimer and can be used for polymerisation of new PLA. The chemical recycling

process that breaks down PLA into lactic acid is called hydrolysis, and requires the presence of water as well as high

temperature. The obtained lactic acid has a high purity and can be polymerised to virgin PLA. This recycled PLA closes the loop and the process may be called a cradle-to-cradle process. The recycling efficiency depends strongly on the operating conditions such as temperature, reaction time and ratio of water to sample [28].

Table 4 shows the influence of the reaction time and Temperature on the recycling efficiency. Furthermore, depending on the temperature, the predominant reaction was recycling to lactic acid (at lower temperatures) or thermal degradation into other low molecular weight carboxylic acids (at higher temperatures).

Table 4- Recycling efficiency of PLLA into lactic acid under various conditions [29]:



Reaction time (min)	Recycling efficiency (%)				
	240 °C	250 °C	260 °C	300 °C	350 °C
5	11.9	21.6	53.9	67.4	55.5
8	35.2	80.1	70.8	71.9	46.7
10	61.7	90.7	84.8	83.8	42.0
15	85.5	91.1	89.2	83.0	30.1
20	–	92.5	91.5	82.5	22.0
30	–	88.4	80.1	79.9	12.7

Biological recycling is another alternative option. The recycled material forms a biomass that binds carbon for a longer period than mechanical recycling or incineration. Biological recycling is usually considered as composting, where microorganisms degrade the organic waste and the degradation products are returned to the natural carbon cycle.

4.5 Mechanical recycling of blends containing bioplastics

Similar to pure bioplastics, the recycling of bioplastic blends has been investigated using both mechanical and chemical recycling methods. Hybrid bioplastics, which refer to blends of bio-based and petro-based polymers, are regarded as more sustainable than pure synthetic polymers because of substituting a part of the petro-based resin by polymers from renewable resources [30]. Apart from the environmental aspects, another advantage of this type of blend is that the limitations in the properties of neat bioplastics are overcome. For example, pure PLA has some drawbacks, such as poor toughness, low impact resistance and poor crystallization behaviour, that limit its current use in food packaging.

Another drawback of PLA is related to its processing in the molten state, and its tendency to undergo thermal degradation. Degradation during processing is related to the processing temperature, the residence time in the extruder and hot runner, and in some cases to the moisture content of the granules. These drawbacks affect also the recyclability of PLA. To overcome the drawbacks of pure PLA, an economically viable strategy is blending PLA with other polymers, because other improvement methods such as copolymerisation of lactic acid with other monomers have not been really successful or commercially viable [31].

For example, blends of PLA and PS have been prepared to balance the cost of PLA and enhance the degradability of PS. The properties of such blends are between the values of pure PLA and pure PS, and have potential application in medical devices and packaging products [32]. Multiple extrusion and injection of a 50/ 50 wt% PLA/PS polymer blend showed that stress and strain at break of the blend decreased sharply after two processing cycles, as shown in Fig. 14, whereas Young's modulus was not significantly affected. After four processing cycles, the Young's modulus showed the minimum reduction by 26%, a larger reduction was observed in the strain at break with 73%, and the largest change was in the stress at break with 79% (all after four processing cycles). The apparent viscosity of PLA/PS blend decreased uniformly with increasing processing number. The compounded PLA/PS blend had an apparent viscosity of 3100 Pa*s, and after each processing cycle, the apparent viscosity of the blend decreased by nearly 15–30%. This behaviour was attributed to the reduction of the molecular weights with the processing cycles [33].

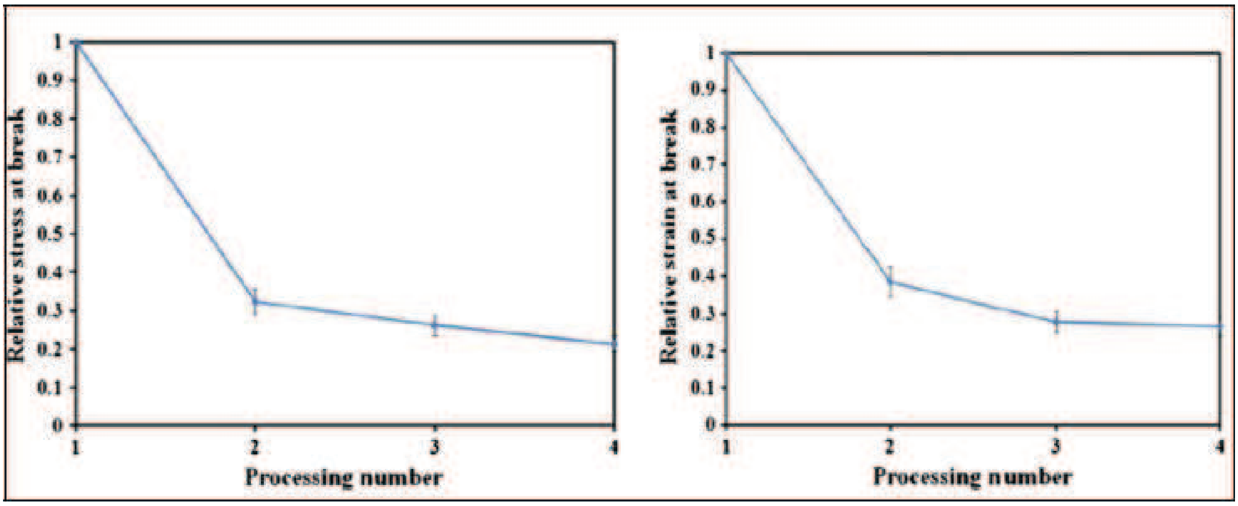
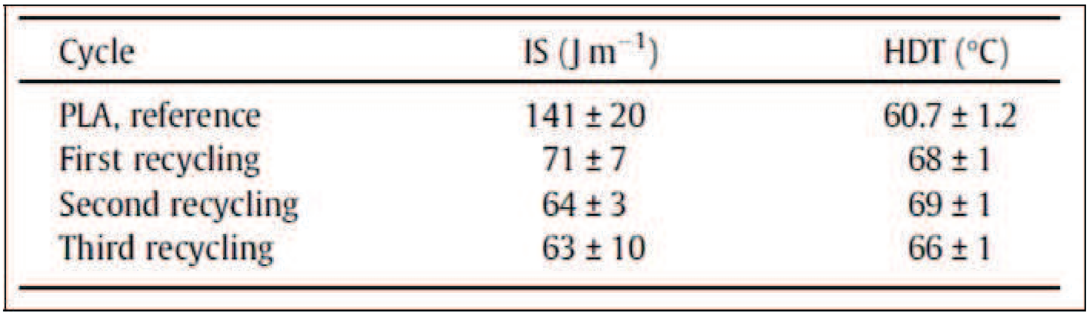


Figure 14-Relative stress at break (a) and relative strain at break (b) versus processing number of PLA/PS blend

Multiple recycling led to a significant reduction in the impact strength (as shown in Table 5), although most of the other mechanical properties were still retained.



Cycle	IS (J m^{-1})	HDT (°C)
PLA, reference	141 ± 20	60.7 ± 1.2
First recycling	71 ± 7	68 ± 1
Second recycling	64 ± 3	69 ± 1
Third recycling	63 ± 10	66 ± 1

Table 5- Izod impact strength (IS) and heat deflection temperature (HDT) values of reference and recycled PLA/PS blend [1]

4.6 Chemical recycling of blends containing bioplastics

Chemical recycling of bioplastic blends has been investigated because of the limitations of the mechanical recycling method, especially the required sorting, thermo- mechanical degradation of polymers and sensitivity to material impurities. For example, PLA and PET cannot be easily or cheaply sorted by sight or by separation methods based on density, which are not efficient enough because of the similar densities of the polymers [34].

On the other hand, industry is concerned about the potential contamination of the PET recycling stream by water bottles made of PLA. It is believed that PLA at even very low contents (any level >0.1% in a PET recycling stream) can act as contamination and seriously affect the properties of the recycled PET. Therefore, PLA needs to be separated from PET before the recycling process starts.

However, even when PLA is separable, it is still problematic because it can increase the cost of recycling by necessitating investment in new sorting equipment. A selective recycling of mixed PLA and PET was studied by depolymerising PLA into a liquid and recovering the unreacted solid PET by filtration. Among three different catalysts tried for the glycolysis of post-consumer PET waste, zinc acetate was the most soluble and effective. Furthermore, for alcoholysis of PLA, zinc acetate could yield an effective depolymerisation of waste PLA (in methanol or ethanol) giving lactate esters, whereas PET remained as an unreacted solid under the same reaction conditions. This is a promising process for the chemical recycling of both neat PLA and mixed PLA/PET, as the separation is facilitated via converting PLA to a liquid monomer from which the solid PET can be filtered. Different routes and the alcoholysis reaction of PLA are presented in Figs. 15 and 16, respectively [35].

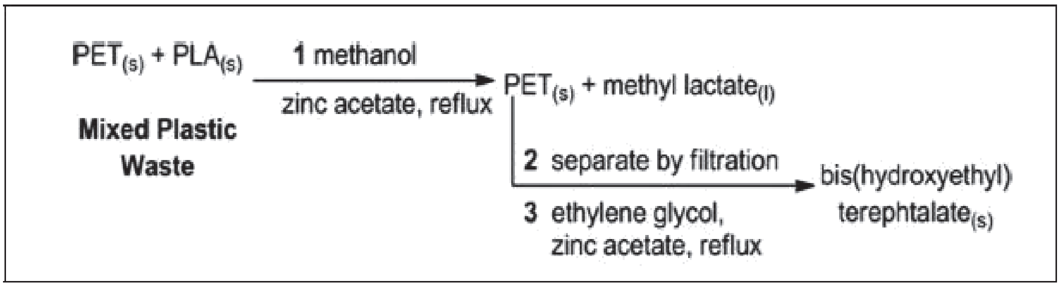


Figure 15-Scheme for the selective recycling of mixed PLA and PET

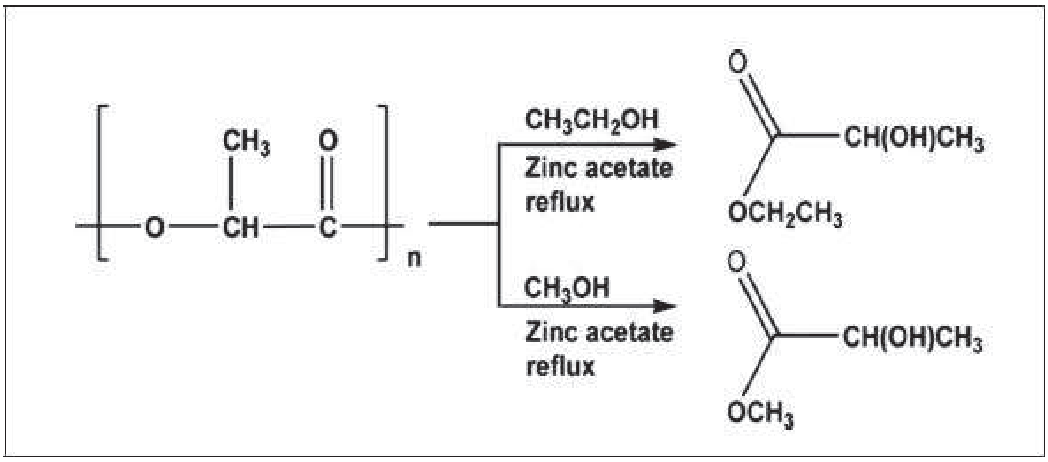


Figure 16-Alcoholysis of PLA

To clarify the influences of other types of plastics as contaminants during chemical recycling, some specific polymer blends were studied. Developing a selective chemical recycling process, blends of PLLA/PE were studied, to be degraded into each of the repolymerisable oligomers using catalysts and enzymes. Two procedures for the selective chemical recycling of PLLA/PE blends were investigated.

The first route was the direct separation of PLLA and PE from the PLLA/PE blend by their solubility in toluene, and then the chemical recycling of PLLA. The second route was the selective degradation of PLLA in PLLA/PE blend forming the lactic acid oligomer [36].

Fig 17 shows the routes to selective recycling of PLLA/ PE blend.

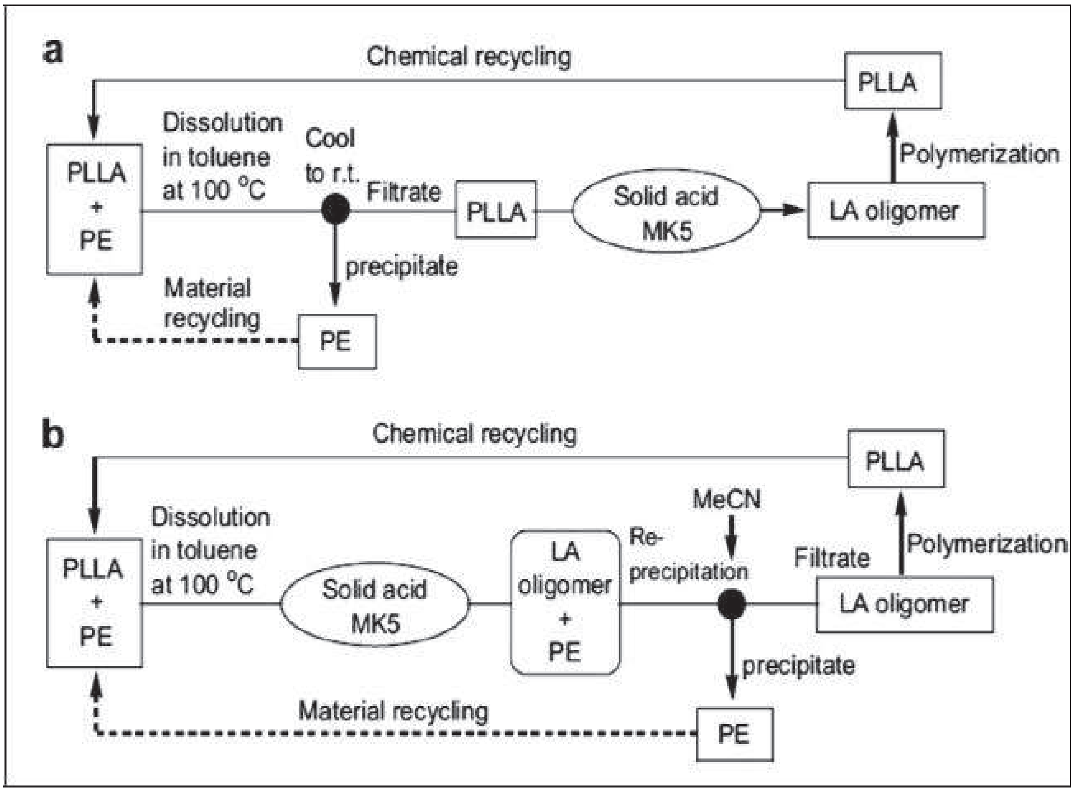


Figure 17-Diagram of selective chemical and material recycling of PLLA/PE blend

4.7 Recycling of biocomposites

Biocomposites are composite materials in which at least one of the constituents is derived from natural resources. Biocomposites cannot easily be called sustainable materials. A sustainable biocomposite should fulfill several requirements:

(1) be manufactured from renewable and/or recycled resources; the synthetic, modification and processing operations should be energy effective and favourable; (3) all the stages of their life cycle should be free of any hazardous environmental or toxicological effects; and (4) have implemented waste management options. Developing biocomposites with a thermoplastic rather than thermoset matrix has been of great interest, mainly because of their recyclability.

Biocomposites based on PLA and flax fibre have been recycled by means of mechanical processing. Compostable flax/PLLA has been shown to have similar mechanical properties to those of glass fibre/PP and superior properties to hemp/PP and sisal/PP composites. After mechanical recycling, as shown in Fig. 18, the tensile properties of biocomposites containing flax fibres at different fibre contents (20% and 30% by weight) are conserved until the third injection cycle. In general, reprocessing resulted in lower molecular weight, reduction of fibre length and separation of fibre bundles. However, the biocomposite properties after three cycles (with no added virgin polymer) were promising regarding the recyclability of this material [37].

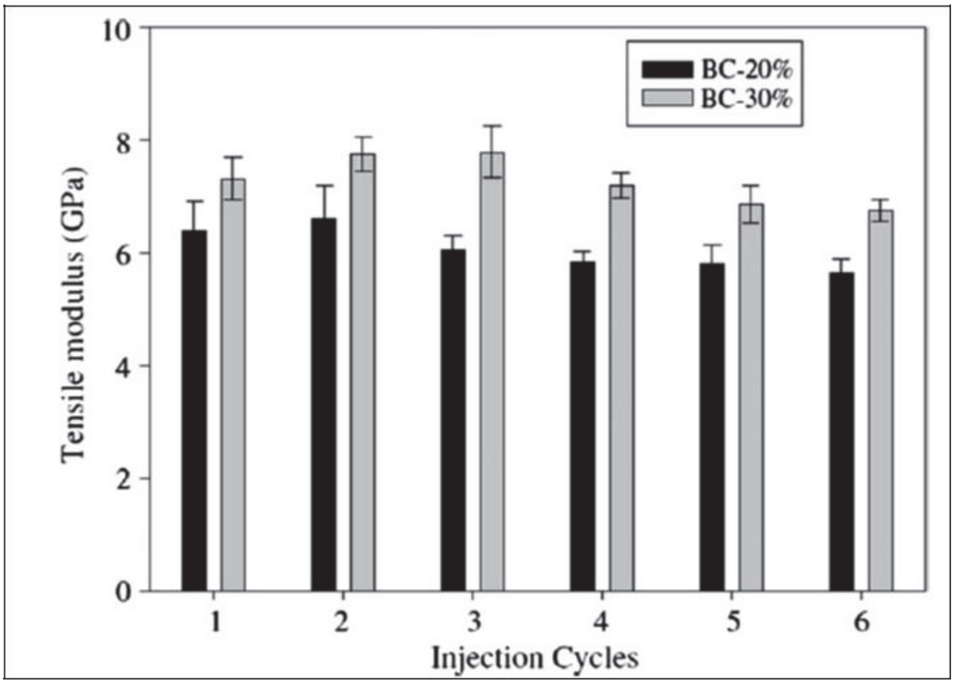


Figure 18-Evolution of tensile strength at yield for PLLA/flax fibre biocomposites containing 20% fibre (BC-20%) and 30% fibre (BC-30%) as a function of injection cycles.

Scanning electron microscopy (SEM) images in Fig. 19 show the tensile fracture surfaces, which give qualitative information about dispersion and orientation of fibres. After the first injection cycle, many bundles of fibres can be noted (Fig. 3.12a), whereas after six injection cycles a more homogeneous fracture surface is observed (Fig. 3.12b).

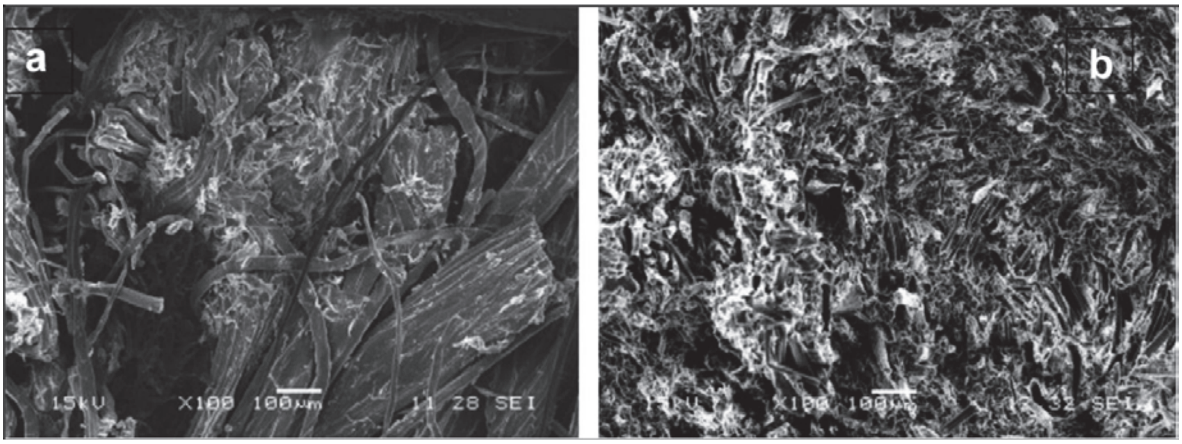


Figure 19- SEM micrograph of the fracture surface of PLLA/flax (80/20 wt%); (a): after one injection; (b): after six injections

PLA/flax composites have their main application in the automotive industry. The mechanical recycling of PLA/flax has led to a decrease in the tensile strength (23%), impact strength (8%) and E-modulus (5%), as well as a corresponding decrease in the PLA molar mass. Furthermore, the recycled composites have potential use as construction materials for indoor applications because the flexural strength and modulus of these materials are comparable to those of conventional formaldehyde wood medium-density fibreboards.

Generally, it is expected that biopolymer-reinforced composites have less recyclability than their neat thermoplastic matrix, because composites are more sensitive to thermomechanical degradation. That is why composting is supposed to be the main waste management route for such materials [38].

In general, the recyclability of natural-filler-reinforced biocomposites (based on either a synthetic or a biopolymeric thermoplastic matrix) is usually guaranteed up to several reprocessing cycles to have preserved mechanical properties. Multiple processing may even enhance the interfacial adhesion between fillers and matrix, resulting in a reported increase in thermal stability in the reprocessed biocomposites. However, different degradative effects can happen because of repeated recycling of biocomposites, such as fibre length reduction and chain scission in the synthetic thermoplastic matrix, which leads to a decrease in the molecular weight and an increase in crystallinity [39].

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Chapter 5 Experimental section

In the introduction we described the structure and applications of eco-composites referring both to natural fiber reinforced composites and natural filled polymers. In the experimental part we start by analyzing a commercial lignin based material named ArboformLV100 by Tecnaro. The LV100 is claimed to be fully based on lignin and is market as “liquid wood”. In the following we present the results of the structural analysis of LV100 and, based on these results, we discuss the formulation of a blend of PLA and lignin developed in our laboratory. Additional results on PP blended with LV100 are presented. The developed recyclable bioepoxy based composites are also presented.

The chapter is organized with the first 4 sections (from 5.1 to 5.4) describing the materials, the processing techniques and the characterization techniques used. The last section (5.5) is devoted to the presentation of the results for each system used. This latter section refers to the papers co-authored during the PhD work.

5.1 Materials

5.1.1 LV 100

The polymer ARBOFORM® LV100 (Fig. 20) furnished by TECNARO™ GmbH which is a spin-off of the Fraunhofer Institute for Chemical Technology (ICT). ARBOFORM®, also known as liquid wood (arbor, Latin = the tree) is a product based on the renewable raw material lignin, which plays a role in the growth process of trees, helping ensure that they lignify and develop stability.

Figure 20-LV pellet

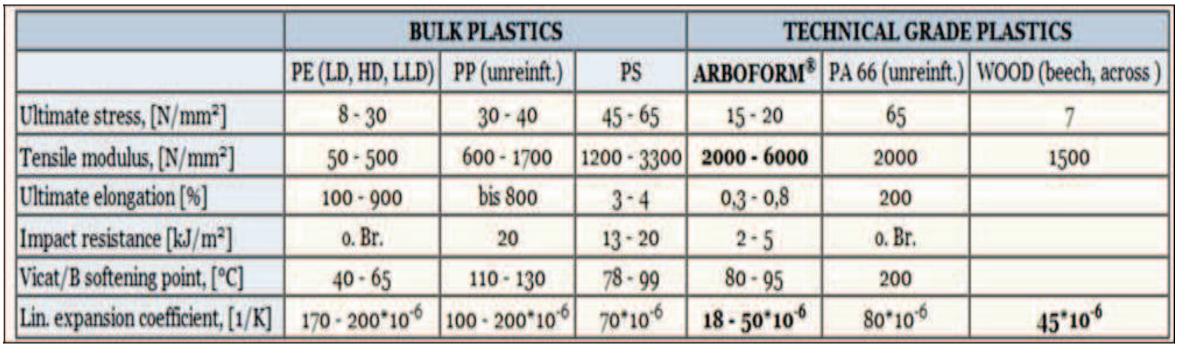
The identical coefficient of thermal expansion of ARBOFORM® and the natural wood makes ARBOFORM® an ideal substrate for veneering wood. Which means that even with temperature variations between -30°C and +90°C there is no risk of delamination.

The maximum possible consistency of quality, together with its material properties, make ARBOFORM® predestined for applications that combine the limitless mouldability of thermoplastics with the characteristics of wood. Among these are the natural appearance and the fact that wood is warm to the touch, important for example when building furniture or musical instruments. In other applications, the expansion properties of ARBOFORM® play an important role, such as veneer wood substrates for car interiors. Incidentally, like naturally grown wood, ARBOFORM® products are 100% biodegradable. ARBOFORM® products are disposed as for naturally grown wood.

	ARBOFORM®
Raw materials	• Lignin • Natural fibres • Natural additives
From renewable raw materials	100 %
Bio-degradability	100 %
Features	• combines all properties of naturally-grown wood • unique worldwide, and protected by patents

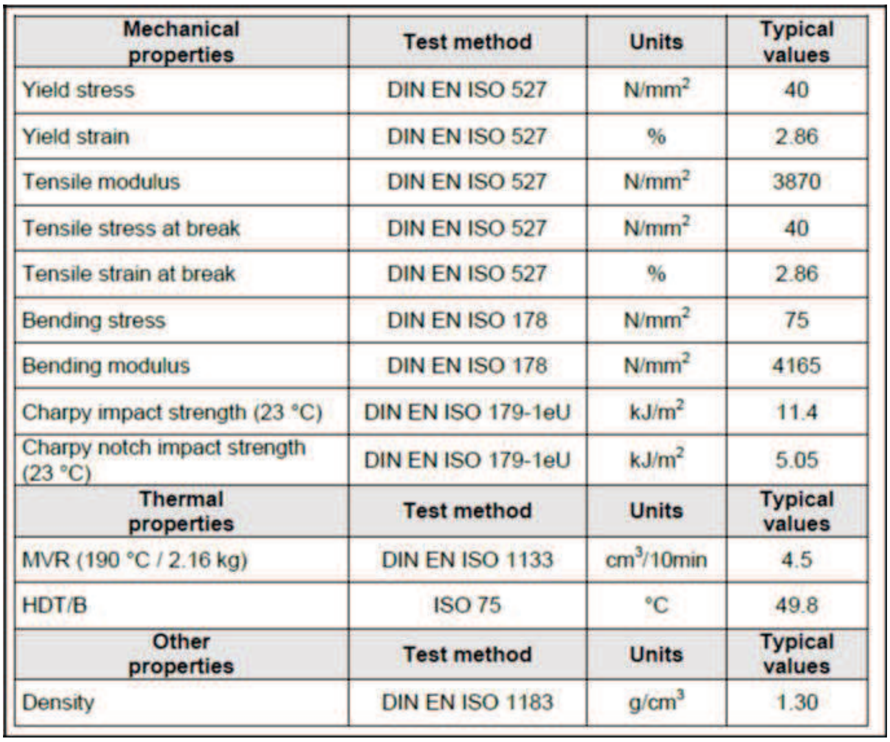
The mechanical and physical properties of both this product and bulk plastics are presented in the following tables where the second one shows the material data of ARBOFORM® LV100 natural given by TECNARO™ GmbH.

Table 6- Mechanical and physical properties of ARBOFORM® and some bulk plastics.



	BULK PLASTICS			TECHNICAL GRADE PLASTICS		
	PE (LD, HD, LLD)	PP (unreinft.)	PS	**ARBOFORM®**	PA 66 (unreinft.)	WOOD (beech, across)
Ultimate stress, [N/mm²]	8 - 30	30 - 40	45 - 65	15 - 20	65	7
Tensile modulus, [N/mm²]	50 - 500	600 - 1700	1200 - 3300	**2000 - 6000**	2000	1500
Ultimate elongation [%]	100 - 900	bis 800	3 - 4	0,3 - 0,8	200	
Impact resistance [kJ/m²]	o. Br.	20	13 - 20	2 - 5	o. Br.	
Vicat/B softening point, [°C]	40 - 65	110 - 130	78 - 99	80 - 95	200	
Lin. expansion coefficient, [1/K]	170 - 200*10^{-6}	100 - 200*10^{-6}	70*10^{-6}	**18 - 50*10^{-6}**	80*10^{-6}	**45*10^{-6}**

Table 7- Mechanical, thermal and physical properties of ARBOFORM® LV100 natural furnished by TECNARO™ GmbH



Mechanical properties	Test method	Units	Typical values
Yield stress	DIN EN ISO 527	N/mm²	40
Yield strain	DIN EN ISO 527	%	2.86
Tensile modulus	DIN EN ISO 527	N/mm²	3870
Tensile stress at break	DIN EN ISO 527	N/mm²	40
Tensile strain at break	DIN EN ISO 527	%	2.86
Bending stress	DIN EN ISO 178	N/mm²	75
Bending modulus	DIN EN ISO 178	N/mm²	4165
Charpy impact strength (23 °C)	DIN EN ISO 179-1eU	kJ/m²	11.4
Charpy notch impact strength (23 °C)	DIN EN ISO 179-1eU	kJ/m²	5.05
Thermal properties	**Test method**	**Units**	**Typical values**
MVR (190 °C / 2.16 kg)	DIN EN ISO 1133	cm³/10min	4.5
HDT/B	ISO 75	°C	49.8
Other properties	**Test method**	**Units**	**Typical values**
Density	DIN EN ISO 1183	g/cm³	1.30

Moreover, compared to ordinary plastic or wood, Liquid Wood has far superior acoustic properties and provides a seemingly endless array of geometric possibilities. Liquid Wood can be used to shape the earcups to more closely resemble the human ear, thereby providing a more complete and comfortable fit, reducing stress on the listener's head and ears.

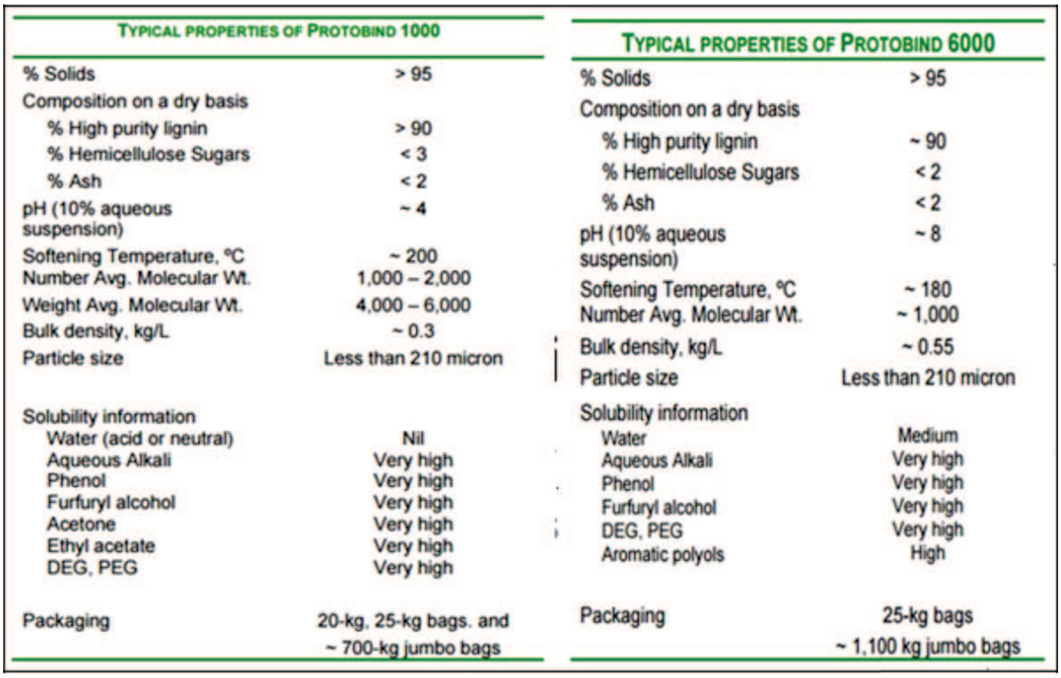
The applications of ARBOFORM® are different (Fig. 21):

- Automotive
- Additive Manufacturing
- Building
- Electrical device
- Furniture
- Toys; Garden

Figure 21-Applications of ARBOFORM®

5.1.2 Lignin

Three types of lignin (Protobind 1000, Protobind 6000, and Protobind 2400) were obtained from Greenvalue (Fig. 22).

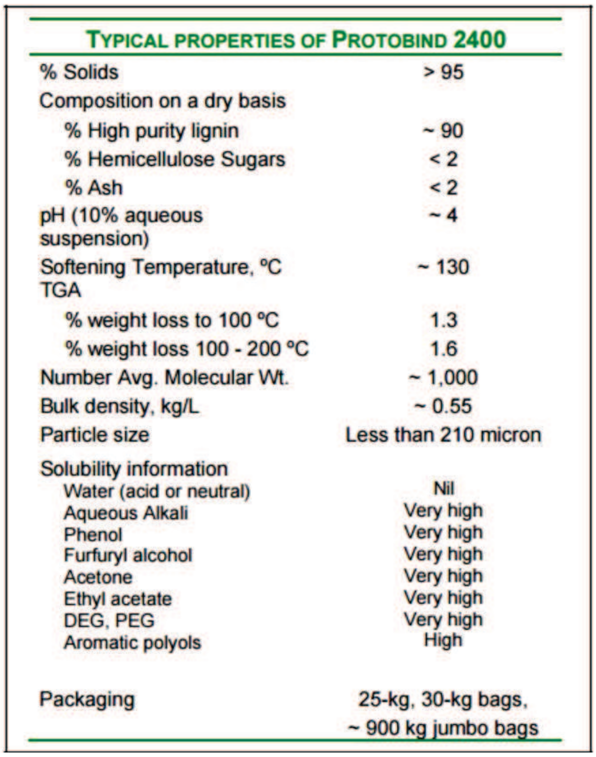


TYPICAL PROPERTIES OF PROTOBIND 1000

% Solids	> 95
Composition on a dry basis	
% High purity lignin	> 90
% Hemicellulose Sugars	< 3
% Ash	< 2
pH (10% aqueous suspension)	~ 4
Softening Temperature, °C	~ 200
Number Avg. Molecular Wt.	1,000 – 2,000
Weight Avg. Molecular Wt.	4,000 – 6,000
Bulk density, kg/L	~ 0.3
Particle size	Less than 210 micron
Solubility information	
Water (acid or neutral)	Nil
Aqueous Alkali	Very high
Phenol	Very high
Furfuryl alcohol	Very high
Acetone	Very high
Ethyl acetate	Very high
DEG, PEG	Very high
Packaging	20-kg, 25-kg bags. and ~ 700-kg jumbo bags

TYPICAL PROPERTIES OF PROTOBIND 6000

% Solids	> 95
Composition on a dry basis	
% High purity lignin	~ 90
% Hemicellulose Sugars	< 2
% Ash	< 2
pH (10% aqueous suspension)	~ 8
Softening Temperature, °C	~ 180
Number Avg. Molecular Wt.	~ 1,000
Bulk density, kg/L	~ 0.55
Particle size	Less than 210 micron
Solubility information	
Water	Medium
Aqueous Alkali	Very high
Phenol	Very high
Furfuryl alcohol	Very high
DEG, PEG	Very high
Aromatic polyols	High
Packaging	25-kg bags ~ 1,100 kg jumbo bags



TYPICAL PROPERTIES OF PROTOBIND 2400

% Solids	> 95
Composition on a dry basis	
% High purity lignin	~ 90
% Hemicellulose Sugars	< 2
% Ash	< 2
pH (10% aqueous suspension)	~ 4
Softening Temperature, °C	~ 130
TGA	
% weight loss to 100 °C	1.3
% weight loss 100 - 200 °C	1.6
Number Avg. Molecular Wt.	~ 1,000
Bulk density, kg/L	~ 0.55
Particle size	Less than 210 micron
Solubility information	
Water (acid or neutral)	Nil
Aqueous Alkali	Very high
Phenol	Very high
Furfuryl alcohol	Very high
Acetone	Very high
Ethyl acetate	Very high
DEG, PEG	Very high
Aromatic polyols	High
Packaging	25-kg, 30-kg bags, ~ 900 kg jumbo bags

Figure 22-Datasheets Protobind 1000-6000-2400

They differ mostly regarding thermal behavior (softening point) and some solubility characteristics.

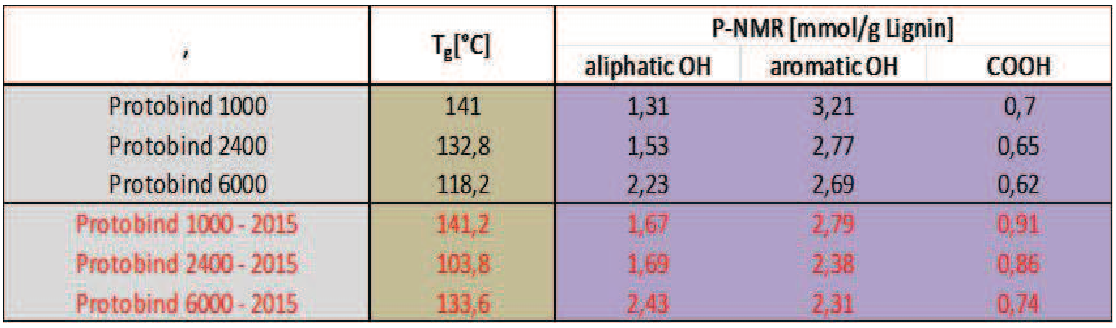
Of these, we have found Protobind 2400 (Fig. 23) to be quite useful as an additive for PLA, showing some improvement in physical properties relative to 100% PLA control, particularly after aging and for its low softening point.

Figure 23-Protobind 2400

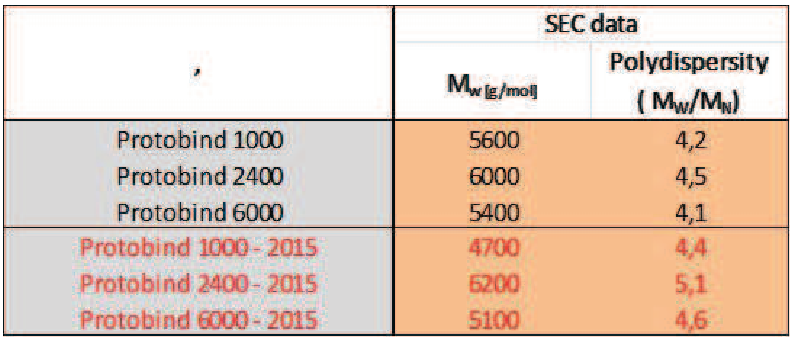
Detailed chemical and thermal analyses of the lignin from Greenvalue were provided from Prof. Bodo Saake (Department of Wood Science, University of Hamburg). The values found vary from year to year (Table 8) .

Table 8- Elementary, T_G, P-NMR, SEC analyses

,	Elementary analysis [%]				
	C	H	O	N	S
Protobind 1000	64,02	5,92	28,65	0,79	0,62
Protobind 2400	62,95	6,32	29,53	0,66	0,54
Protobind 6000	61,93	6,42	28,31	2,65	0,69
Protobind 1000 - 2015	64,71	5,68	27,34	0,92	1,35
Protobind 2400 - 2015	63,07	6,12	28,63	0,75	1,43
Protobind 6000 - 2015	62,5	6,25	27,4	2,41	1,44



,	T_g[°C]	P-NMR [mmol/g Lignin]		
		aliphatic OH	aromatic OH	COOH
Protobind 1000	141	1,31	3,21	0,7
Protobind 2400	132,8	1,53	2,77	0,65
Protobind 6000	118,2	2,23	2,69	0,62
Protobind 1000 - 2015	141,2	1,67	2,79	0,91
Protobind 2400 - 2015	103,8	1,69	2,38	0,86
Protobind 6000 - 2015	133,6	2,43	2,31	0,74



,	SEC data	
	$M_{w\,[g/mol]}$	Polydispersity (M_W/M_N)
Protobind 1000	5600	4,2
Protobind 2400	6000	4,5
Protobind 6000	5400	4,1
Protobind 1000 - 2015	4700	4,4
Protobind 2400 - 2015	6200	5,1
Protobind 6000 - 2015	5100	4,6

5.1.3 PLA 4032D

Poly-L-lactic acid, a typical biodegradable polymer made from corn was used as matrix.

It can be used for thermoformed, coating, injection molded, blow molded, and fiber applications.

PLA 4032 D is supplied by NatureWorks LLC and it is available in pellet form (Fig. 24).

Figure 24- PLA 4032D pellet

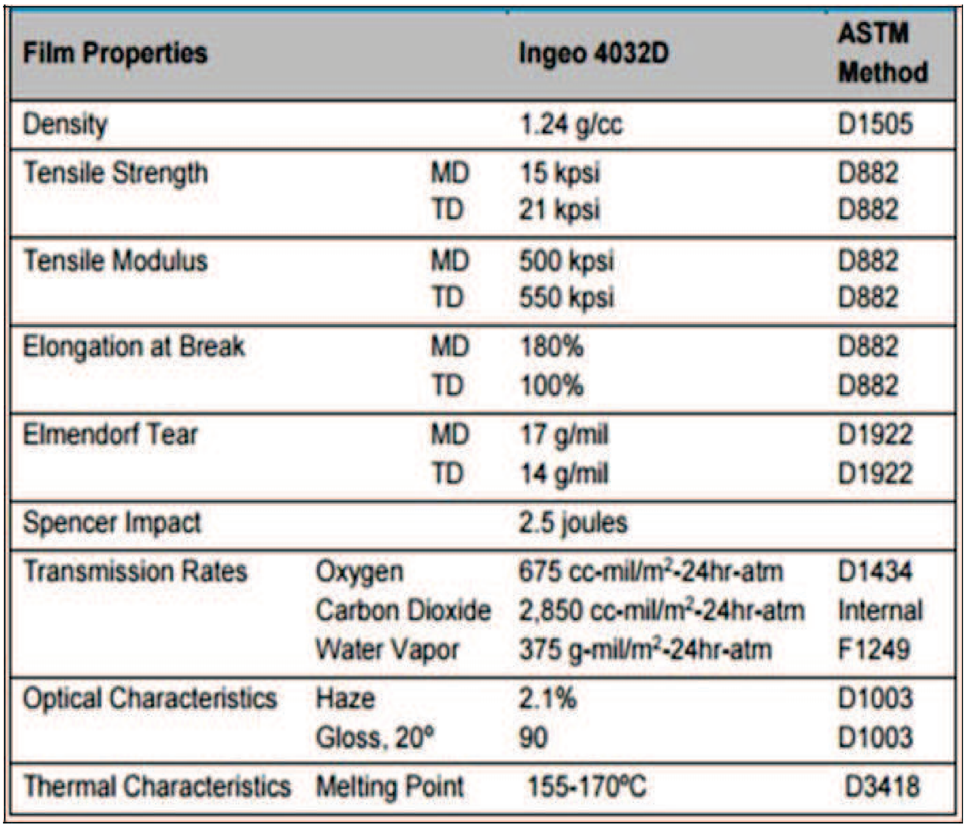
Drying prior to processing is essential. The polymer is stable in the molten state, provided that the extrusion and drying procedures are followed.

It is an ideal product for laminations and other packaging applications. Additional properties include barrier to flavor and grease and oil resistance.

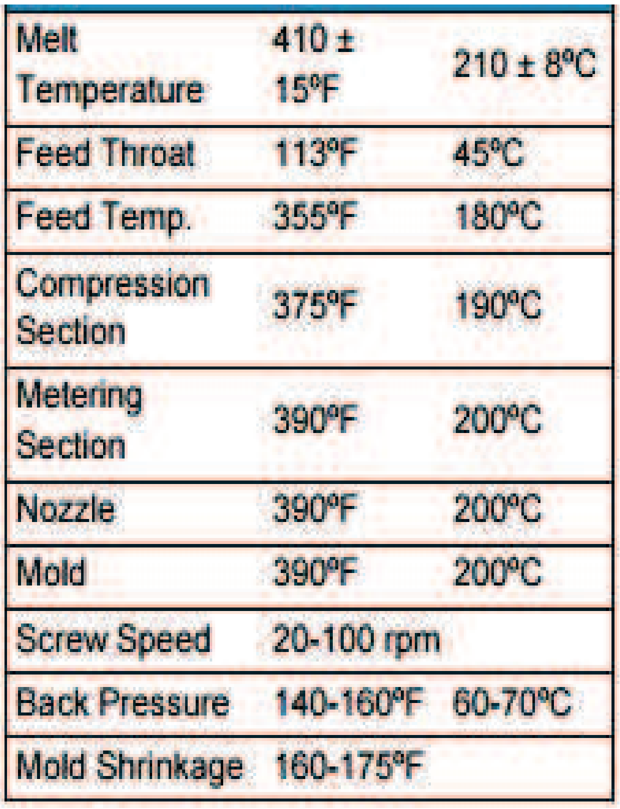
Below are listed the typical values of physical properties of PLA used for the development of this thesis (Table 9).

Table 9- Typical Material & Application Properties and Processing

Temperature Profile.



Film Properties		Ingeo 4032D	ASTM Method
Density		1.24 g/cc	D1505
Tensile Strength	MD	15 kpsi	D882
	TD	21 kpsi	D882
Tensile Modulus	MD	500 kpsi	D882
	TD	550 kpsi	D882
Elongation at Break	MD	180%	D882
	TD	100%	D882
Elmendorf Tear	MD	17 g/mil	D1922
	TD	14 g/mil	D1922
Spencer Impact		2.5 joules	
Transmission Rates	Oxygen	675 cc-mil/m^2-24hr-atm	D1434
	Carbon Dioxide	2,850 cc-mil/m^2-24hr-atm	Internal
	Water Vapor	375 g-mil/m^2-24hr-atm	F1249
Optical Characteristics	Haze	2.1%	D1003
	Gloss, 20°	90	D1003
Thermal Characteristics	Melting Point	155-170ºC	D3418



Melt Temperature	410 ± 15ºF	210 ± 8ºC
Feed Throat	113ºF	45ºC
Feed Temp.	355ºF	180ºC
Compression Section	375ºF	190ºC
Metering Section	390ºF	200ºC
Nozzle	390ºF	200ºC
Mold	390ºF	200ºC
Screw Speed	20-100 rpm	
Back Pressure	140-160ºF	60-70ºC
Mold Shrinkage	160-175ºF	

It is specifically designed general extrusion processes when a higher melting point product is needed. Ingeo biopolymer 4032D is a general purpose extrusion grade that is used naturally or as part of a formulated blend

5.1.4 Epoxy and amine monomers

SuperSap epoxy monomers CLX(S) and the cure inhibitor INH by Entropy Resins were mixed with the Recyclamine® 301 by Connora Technologies. The inhibitor was added in the percentage of 25% to the epoxy monomer to have a pot life of 90 min at 25 °C. The CLX(S) monomer is composed of epoxidized pine oils, bisphenol A/F type epoxy resin, benzyl alcohol, and proprietary reactive epoxy diluents. The Recyclamine® 301 is a cleavable polyamine ether patented by Connora Technology.

5.1.5 Reinforcement Fabrics

The carbon fabric used was a twill fabric of T300 carbon fibers with 200 gsm (grams per square meter) areal weight purchased from Prochima, Italy. Flax fabrics (400 gsm, twill) were purchased by Composites Evolution (UK).

5.2 Processing techniques

5.2.1 Thermoplastic specimens processing techniques

The purpose of this thesis is to investigate the behavior of liquid wood and to develop in our laboratory novel composites with a matrix consisting of a mixture of PLA and lignin for novel applications (i.e. injection molding and additive manufacturing).

Before blends preparation, PLA pellets and lignin powder were dried in a vacuum oven for 24 h at 60 °C.

The first phase of the experimentation is given by the mixing of the PLA 4032D with Protobind 2400 and then LV 100.

A mixing temperature equal to 190 °C was chosen, since, above this temperature, LV100 would be degraded damaging the characteristics of the final material.

The mixing is carried out using a machine called Brabender$^{\text{TM}}$ (Fig. 25).

Figure 25-Brabender mixer

The Brabender mixer is composed of three main parts:

a) a mixing chamber;

b) a thermostat for temperature control;

c) a device for setting and checking the speed of the rotors within the mixing chamber (Fig. 26).

Figure 26-A detail of the mixing chamber

The chamber is formed by a cavity within which the two rotors rotate in the opposite direction. The blades are made of special steel. Counter-rotation towards each other at different speeds provides excellent compounding and mixing characteristics at an adjustable rate expressed in number of revolutions per minute (*rpm*). Heating/cooling is done either through a cold circulation thermostat or electrically with air cooling since the temperature is measured by a thermocouple and can be set through the control thermostat. The instrument is interfaced to a computer and by means of a software it is possible to set some parameters following the time course of torque (a magnitude related to the viscosity of the reaction mass in the molten state) and the temperature during reactions. The Torque is the main indicator for monitoring the behavior of the material during mixing. Moreover, starting from variations in torque, one can obtain information on any degradation processes suffered by the polymeric material during mixing.The torque is an indirect measure for the viscosity of the melt.

The torque measurements were taken after 5min the ramp to 190°C ended to ensure uniform temperature of the melt. This time is assumed as T0 in our test (all the samples referred as T0 were collected opening the mixing chamber after 5min at the end of the ramp up to 190°C which followed the premixing at 160°C). The test lasted for 20min after temperature equilibration (i.e. T0) and the chamber was then opened to extract the sample referred as T20.

The testing procedure is reported below:

The blend PLA and Protobind were prepared varying the amount by weight of Protobind: 10wt%, 25wt% and 35wt%.

The amount of material to be inserted into the mixing chamber was equal to 45 g for blends and 70g for LV100.

The first test was performed by mixing 4,5 g of lignin with 39,5 g of PLA since it was considered a weight percentage of 10% for lignin and 90% for PLA. The counter-rotating blades were placed in rotation to the rotation speed of 50 rpm. The second test was performed with the following weight percentages: 25% Lignin and 75% PLA that expressed in grams are equal to 11,25 g of Lignin and 33,75 g of PLA. The other characteristics of the test have been left unchanged. The third test was performed with the following weight percentages: 35% lignin and 65% PLA that is 15,75 g of lignin and 29,25 g of PLA with the other features of the test left unchanged. The fourth test was performed by mixing only 45g of PLA and another test was performed only LV 100 (70g). The samples prepared are reported in Table 10.

Table 10- Samples prepared in the mixer

Samples	**T0**	**T20**
PLA+10%Protobind	5 minutes at 160°C 5minutes at 190°C	5 minutes at 160°C 20minutes at 190°C
PLA+10%Protobind	5 minutes at 160°C 5minutes at 190°C	5 minutes at 160°C 20minutes at 190°C
PLA+10%Protobind	5 minutes at 160°C 5minutes at 190°C	5 minutes at 160°C 20minutes at 190°C
PLA	5 minutes at 160°C 5minutes at 190°C	5 minutes at 160°C 20minutes at 190°C
LV 100	5 minutes at 160°C 5minutes at 190°C	5 minutes at 160°C 20minutes at 190°C

The resulting blends are showed in Fig. 27.

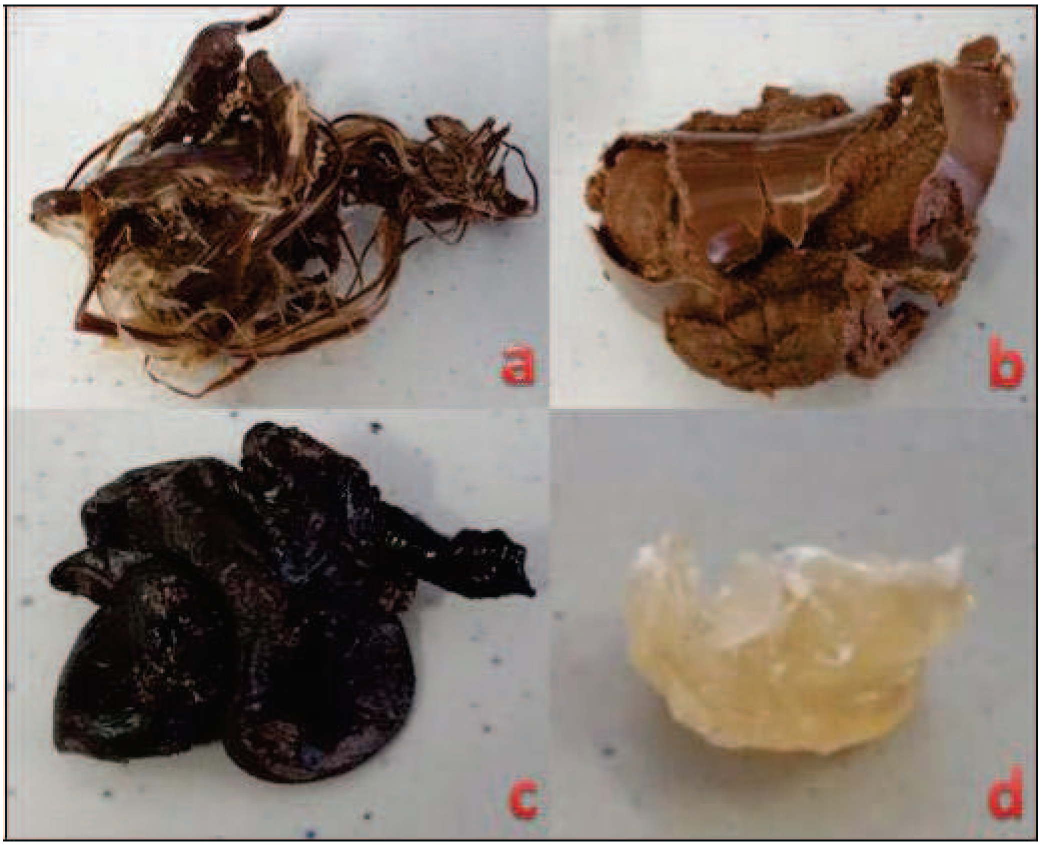


Figure 27-Blends T0 ***a)****PLA+10%LG* ***b)*** *LV* ***c)*** *PLA+25%LG* ***d)*** *PLA*

5.3 Extraction from thermoplastic composites

To fulfill the characterization of degradation products after processing solvent extraction to separate PLA from lignin was carried out. This procedure is needed in order to separate the polymeric soluble fraction from the natural filler. This procedure then allowed to obtain products which can be further analyzed by chemical techniques like NMR and GPC to fully understand the degradation reactions occurring during processing.

5.3.1 Extraction using $CHCl_3$

The extraction process involves combining the blends and LV untreated (pellets) with Chloroform ($CHCl_3$) in a ratio 1:20mL, stirring for 24h. Then the compounds were filtered under vacuum and the two extracts were dried (Figs. 28-29).

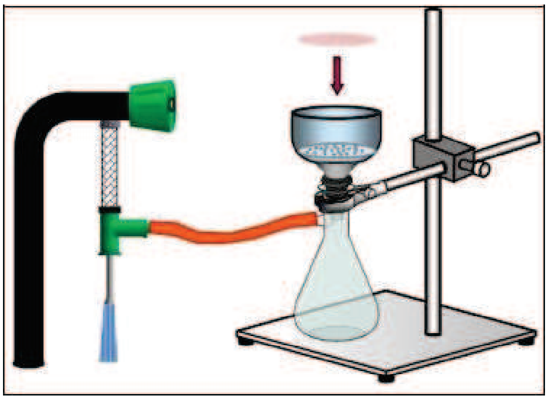


Figure 28-Apparatus for filtration under vacuum

Figure 29-Filtration under vacuum of LV pellets

The Fig. 30 shows two extracts from LV100 pellets.

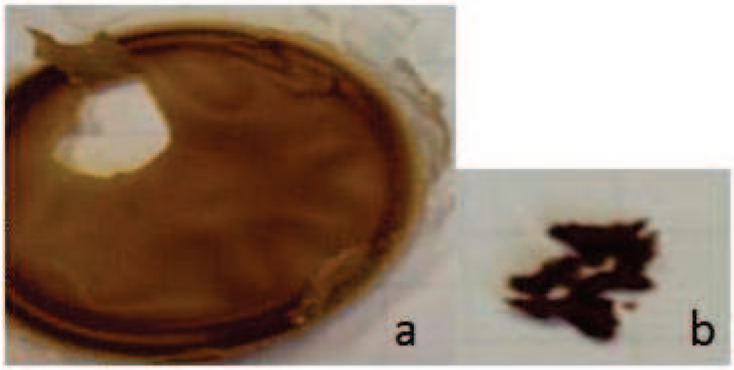


Figure 30-Two extracts from LV pellets using $CHCl_3$ (a) PLA (b) Lignin

The samples extracted and initial quantities are reported in Table 11.

Table 11- Samples extracted

Sample	**Mix conditions**	**Initial quantities**	**Extract**
LV	T20	M=3,0582 g + 60 ml $CHCl_3$	YES *(PLA_e = 1,8084 g)* *($Lignin_e$= 0,3702 g)*
LV	untreated	M=3,2726 g + 60 ml $CHCl_3$	YES (PLA_e = 2,3563 g) ($Lignin_e$= 0,5329 g)
LV	T0	M = 3,1696 g + 60 ml $CHCl_3$	YES (PLA_e = 2,8597 g) ($Lignin_e$=0,2659 g)
PLA+10% Protobind 2400	T20	M = 3,1803 g + 60 ml $CHCl_3$	YES (PLA_e = 2,1729 g) ($Lignin_e$ = 0,1954 g)
PLA+10% Protobind 2400	T0	M = 5,1017 g + 100 ml $CHCl_3$	YES PLA_e = 2,1409 g) ($Lignin_e$ = 0,1053 g)
PLA+25% Protobind 2400	T20	M = 3,1982 g + 60 ml $CHCl_3$	YES (PLA_e =3,0879 g)

			(Lignin$_e$ = 0,1821 g)
PLA+25% Protobind 2400	T0	M = 3,1080 g + 60 ml $CHCl_3$	YES (PLA$_e$ = 2,6240 g) (Lignin$_e$ = 0,5740 g)
PLA+35% Protobind 2400	T20	M = 3,2050 g + 60 ml $CHCl_3$	YES (PLA$_e$ = 2,5023 g) (Lignin$_e$ = 0,7150 g)
PLA+35% Protobind 2400	T0	M = 3,0003 g + 60 ml $CHCl_3$	YES (PLA$_e$ = 1,9803 g) (Lignin$_e$ = 0,9503 g)

5.3.2 Extraction using THF and EtOH

The separation process involves combining the blends with THF, followed by heating (at 60°C for 1day) and agitation. The THF is used to solubilize the blends and then the compounds are centrifuged (at 4000 rpm for 20 minutes). The soluble fraction is drawn out and the ethanol is added. To enhance the purification the temperature of the solution is lowered; in fact the solution is placed in the cooling unit for 30 minutes. After the filtration the extracts are dried; in particular the PLA is dried at 60°C for 1 day in the heater. To remove the solvent from the lignin the rotavapor is used and then the lignin is dried at 60°C for 1 day in the heater (Fig. 31).

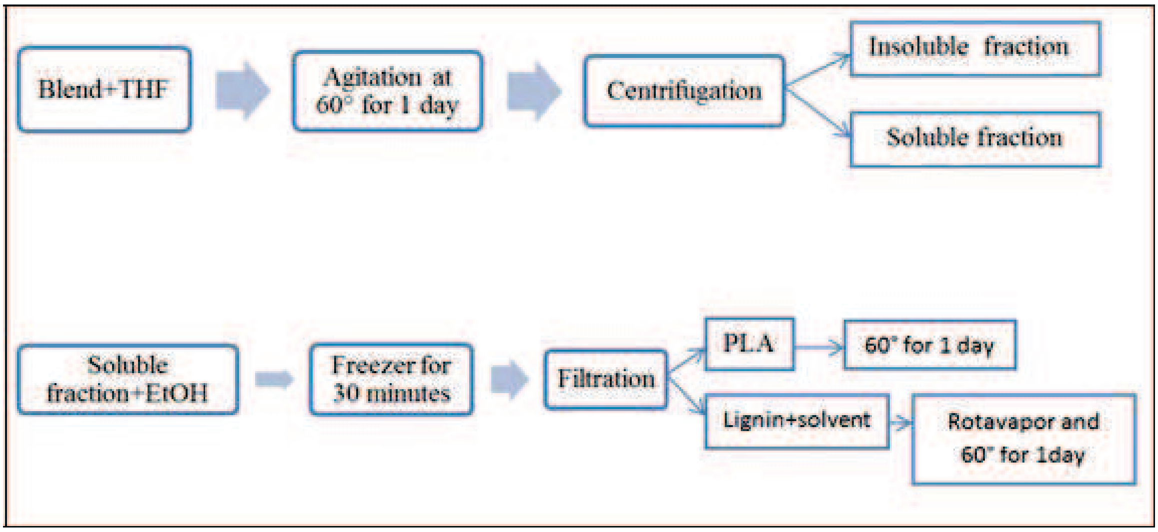


Figure 31-Scheme of extraction

In the following Fig. 32 shows two extracts from LV100 pellets. The samples extracted and initial quantities are reported in Table 12.

Figure 32-Two extracts from LV pellets using THF and EtOH (a) PLA (b) Lignin

Table 12- Samples extracted

Sample	***Mix conditions***	***Initial quantities***	***Extract***
LV	T20	M=0,5000 g + 20 ml THF+80ml EtOH	YES *(PLA$_e$ = 0,2990 g)* *(Lignin$_e$= 0,0473 g)* *(Insoluble fraction in THF=0,0954 g)*
LV	T0	M=0,5091 g + 20 ml THF+80ml EtOH	YES (PLA$_e$ = 0,3262 g) (Lignin$_e$=0,0062 g) *(Insoluble fraction in THF=0,1002 g)*
PLA+10% Protobind 2400	T20	M=0,5010 g + 20 ml THF+80ml EtOH	YES (PLA$_e$ = 0,3629 g) (Lignin$_e$ = 0,0469 g) *(Insoluble fraction in THF=0,0754g)*
PLA+10% Protobind 2400	T0	M=0,5230 g + 20 ml THF+80ml EtOH	YES PLA$_e$ = 0,3825 g) (Lignin$_e$ = 0,0453 g) *(Insoluble fraction in THF=0,0631 g)*
PLA+25% Protobind 2400	T20	M=0,5023 g + 20 ml THF+80ml EtOH	YES (PLA$_e$ =0,3078 g) (Lignin$_e$ = 0,1000 g) *(Insoluble fraction in THF=0,0893 g)*
PLA+25% Protobind 2400	T0	M=0,5266 g + 20 ml THF+80ml EtOH	YES (PLA$_e$ = 0,3540 g) (Lignin$_e$ = 0,1026 g) *(Insoluble fraction in THF=0,0631g)*
PLA+35% Protobind 2400	T20	M=0,5225 g + 20 ml THF+80ml EtOH	YES (PLA$_e$ = 0,2568 g) (Lignin$_e$ = 0,1492 g) *(Insoluble fraction in THF=0,2215g)*
PLA+35% Protobind 2400	T0	M=0,5063 g + 20 ml THF+80ml EtOH	YES (PLA$_e$ = 0,2569 g) (Lignin$_e$ = 0,1537 g) *(Insoluble fraction in THF=0,0576g)*

5.4 Thermoset specimens processing techniques

5.4.1 HP-RTM composite manufacturing

The HP-RTM manufacturing was carried out at the Cannon Afros plant using a press (capacity 1000 t) with the high pressure metering equipment used for the tanks (Fig.33). The epoxy monomer was heated to 80 °C and pressurized to 160 bar. The amine was kept at room temperature and pressurized at 160 bar. Before starting the resin injection the carbon fabrics were cut and placed in the mould preheated to 120 °C. The mould was closed and vacuum was applied to remove excess air. Once the mould was degassed, the vacuum was shut off and injection started. The epoxy monomer and the amine were mixed (100:25 Epoxy:Amine) in the impingement head and the resulting mixture injected in the mould. When mould internal pressure reached the value of 50 bar resin injection was stopped. Injection time was 25 s. The panel was left to cure at 120 °C for 5 min. The mould used for the trials is an omega shaped mould with one central injection point. Several lay ups were used varying the reinforcements as reported in Table 13. The panels were cured at 120 °C for different times from 5 to 15 min

Figure 33- Cannon Afros plant used for HP-RTM trials (1000tons press and high pressure metering mixing unit).

Table 13- Lay up and curinng times tested

Fabric	Lay up	Curing time/min
Biotex	4NF	8
Carbon 200	8CF	8
Hybrid	1NF/6CF/1NF	8
Hybrid	5CF/2NF/3CF	8
Biotex	4NF-5	5
Biotex	4NF-15	15

5.4.2 HP-RTM composite recycling and reprocessing

A sample (6.55 gr) of cured composite was treated with 300 mL of acetic solution (25 volume % of acetic acid) at 80 °C for 1.5 hours. The mixture was then filtered and the CFs separated from the liquid phase. CFs were allowed to dry and weighed (3 gr). The acetic solution was neutralised with a NaOH (pH=10) until a solid precipitate appeared. The mixture was cooled and filtered. The solid was washed in distilled water at about 40 °C. The solid dissolved again. Few drops of NaOH solution were added and a white solid precipitated from the solution, an epoxy thermoplastic polymer. The chemical process is reported in Figure 34. The epoxy thermoplastic was further processed into dogbone specimens using a micro injection moulding machine (Xplore micro injection moulder IM 12 by DSM) heating the polymer at 190 °C and injecting it at 16 bar in a

mould kept at 50°C.

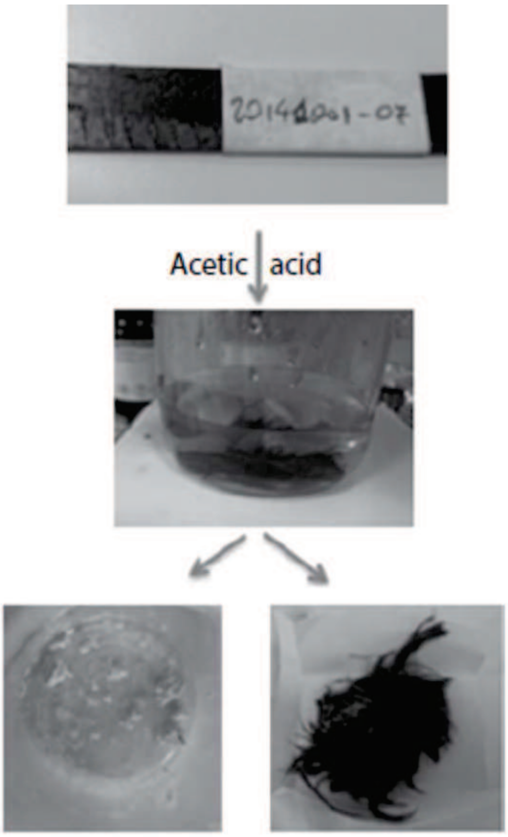


Figure 34- Scheme of chemical recycling of cured composites.

5.5 Results and discussions

This section reports the main results obtained by the characterization of the prepared blends and composites. The section is organized in four sub sections focused on each type of blend or composite obtained from experimental investigation. The first three subsections refer to the thermoplastic blends studied while the last sections refer to the biobased thermoset systems developed. The results are presented and thoroughly discussed while the general conclusions are presented in a last paragraph at the end of this section.

5.5.1 Structure and Thermomechanical Processing of LV1000 Lignin based commercial system

The properties and the structure of the virgin blend will be discussed first. The processing stability of the blend is presented then and discussed in terms of the effects of processing time on the mechanical and thermal properties. The information gained from structure analysis of the blend

are used to discuss the processing stability.

The virgin blend was analyzed by DSC (Fig. 49). The thermogram showed the presence of a glass transition temperature (Tg) at 61.3 °C and two peaks, one exothermic and the other endothermic, at 115.6 and 171.0 °C, respectively. The Tg was further confirmed by the DMA analysis which clearly showed the presence of an a-relaxation peak centered at 67.1 °C for measurements at Hz (Fig. 50). The Tg shift with the frequency observed in Fig. 50 is typical of glass transition relaxations. The presence of a Tg at 61.3 °C (67.1 °C from DMA) is unusual for lignin which is reported in literature to present Tg values varying from 90 to 139 °C [1]. The endothermic peak at 171.0 °C suggested the presence of a major component of the blend melting at about 171.0 °C.

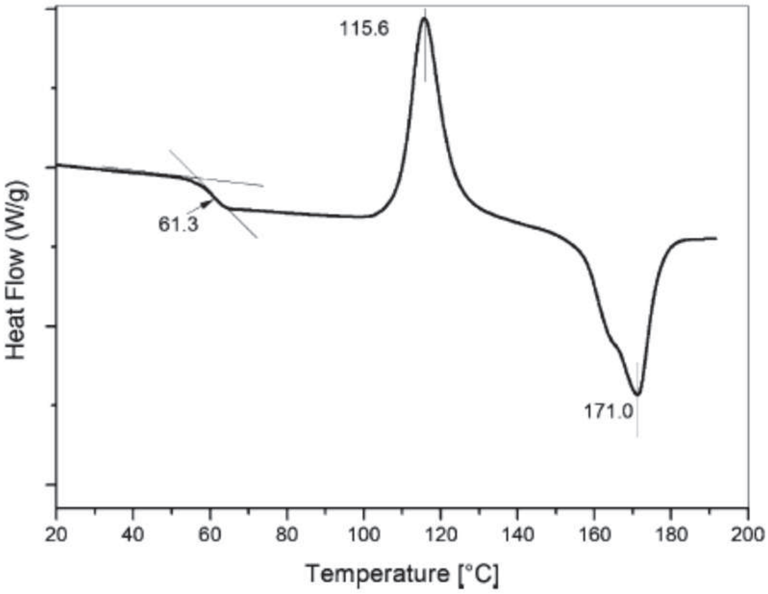


Figure 49- DSC scan of LV1000 (scan run at 20 °C/min in nitrogen)

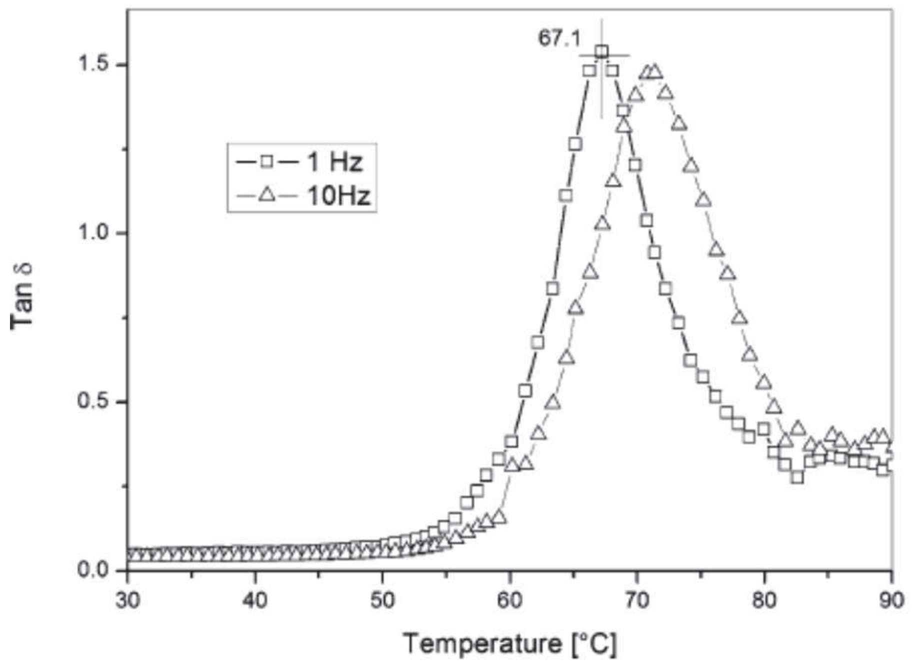


Figure 50- Tanδ versus temperature of LV1000

The results of the thermal analysis of the virgin blend led to the conclusion that the polymer composition contains different components. The brown color of the blend (Fig. 51) was a clear indication of the presence of lignin as a major component. However, the melting behavior suggested the presence of a second component with thermoplastic behavior. To unveil the composition, the virgin blend was fractioned following the procedure reported in experimental section. The fraction soluble in THF accounted for 75 wt% of the total composition. A residual component, insoluble in THF, was recovered for 25 wt% of the total composition. This latter component appeared brown while the first component was white.

Figure 51- Pellets of LV1000

The THF-soluble component was further analyzed by DSC and NMR. The calorimetric curve (Fig. 52) revealed a similar trend to that of the virgin blend (Fig. 49) with a glass transition at 63.2 °C as well as an exothermic and an endothermic at 123.5 and 169.3 °C, respectively. This behavior is typical of PLA. NMR analysis (Fig. 53) confirmed that the PLA constituted the THF soluble fraction, since it shows a quartet centered at 5.15 ppm due to the methyne (C–H) and a doublet at 1.58 ppm due to the methyl (CH_3) of the (L/D) PLA units [2].

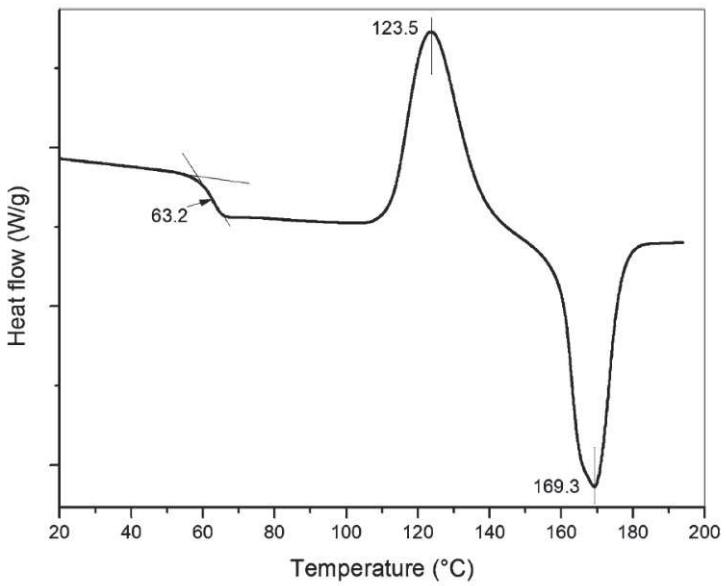


Figure 52- DSC scan of the THF soluble fraction obtained from the virgin blend pellets (scan run at 20 _C/min in nitrogen)

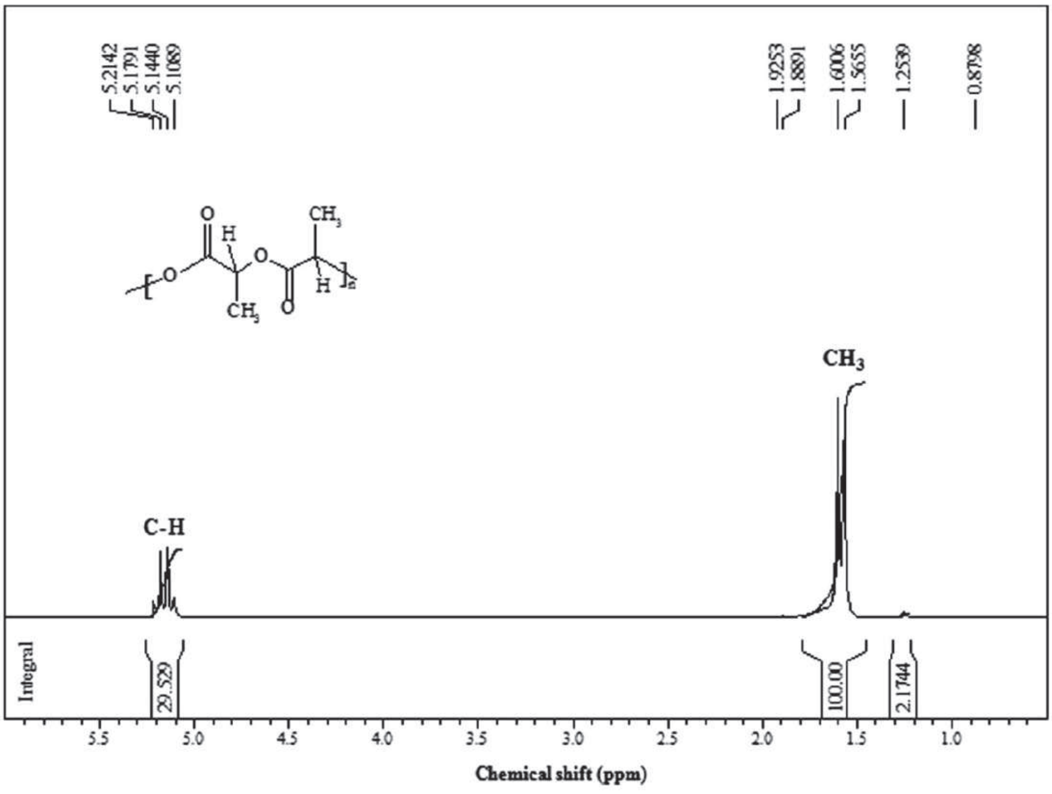


Figure 53 -^{1}H-NMR spectrum of the THF soluble fraction

For further characterization of the insoluble fraction a carbohydrate analysis of the virgin blend was performed after sulfuric acid hydrolysis. The hydrolysis residue was very high and amounted to 86.3 wt%. This residue contained lignin either from wood or as an additional additive. In addition, other hydrolysis stable polymers e.g. PLA are 10.8 wt%. Glucose was the predominant monosaccharide (7.1 wt%) followed by mannose (2.0 wt%), xylose (1.0 wt%), galactose (0.5 wt%), and arabinose (0.2 wt%). Rhamnose was only present in traces. The ratio of the monosaccharides reflects the typical composition of softwood e.g. Norway spruce, with galactoglucomannan and arabinoxylan as major hemicelluloses besides the cellulose [3]. This compositional ratio indicates that the raw material was not subjected to a strong chemical treatment and that ground wood was incorporated into the blend. This material would still contain the natural lignin content of the tree. Considering that softwood has a lignin content of about 30 wt% the wood content in the blend can be estimated to be about 15.4 wt%. The 9:1 (v/v) solution of acetone:water can be applied to extract technical lignin which was added to the blend as an additive. Thus this treatment does not remove lignin from the incorporated wood particles but only the additional technical lignin.

From SEC in DMSO LiBr the molar mass and the recovery rate of extracted lignin could be obtained. The sample has a weight average molar mass of 8800 g/mol with a polydispersity index of 6.7. The molar mass distribution exhibits a slight shoulder in the high molar mass distribution and two shoulders in the low molar mass range below 1000 g/mol (Fig. 54).

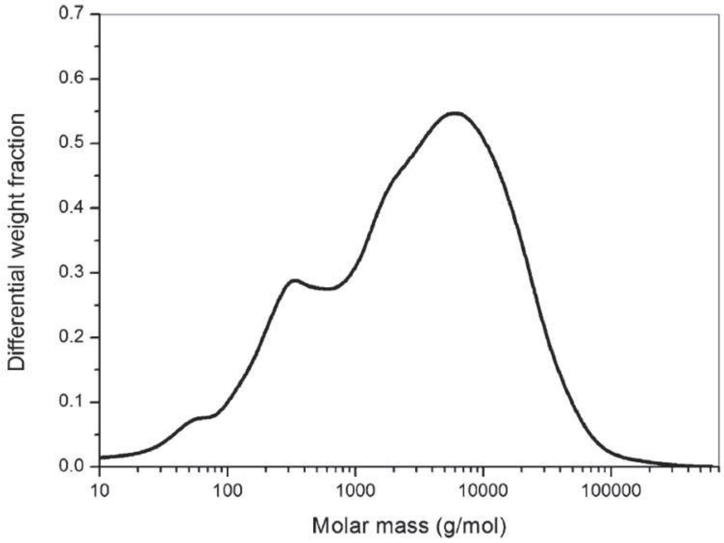
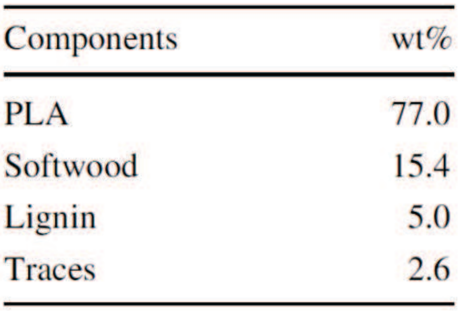


Figure 54- Molar mass distribution of lignin extracted from the virgin blend as determined by SEC in DMSO LiBr

The lignin yield based on the virgin blend was 5.3 wt%. In addition, the extracted lignin was analyzed regarding its elemental composition (C 65.8 %; H 7.3 %, N 0.2 %, S 0.6 %). The sulfur content of 0.6 % is very low for technical lignin. Purified kraft lignin has sulfur contents of 2–3 % while for lignosulfonates 4–8 % sulfur have been reported [4, 5]. Based on these results, the lignin found in the virgin blend could be obtained from the soda process or from organsolv process and steam explosion.

However, to fulfill the annual production rate by Tecnaro (i.e. 5000 t/y) it is most likely that the extracted lignin was an annual plant lignin from the soda process. The determined sulfur and nitrogen may result from the natural raw material e.g. its protein content. Regarding the composition of the blend, it can be concluded that the product contained about 15.4 wt% ground softwood and 5 wt% soda lignin. Subtracting the lignin content (wood *4.5 %; soda lignin *5 %) from the hydrolysis residue the content of other polymers e.g. PLA can be estimated to be around 77 wt%. Other trace components for about 3 % were not identified but they can be presumably organic additives, wax etc. which may be added as processing aids. The final composition of the virgin blend is summarized in Table 14. This result is in good agreement with THF extraction that found a concentration of PLA fraction of 75 wt% in the virgin blend.

Table 14- Compositional analysis of LV1000



Components	wt%
PLA	77.0
Softwood	15.4
Lignin	5.0
Traces	2.6

The processing stability of the blend was first studied monitoring the torque in the batch mixer (Fig. 55). The torque curve (Fig. 55) showed a sudden increase in the first minutes due to polymer pellets loading and melting in the chamber which, because of polymer loading, cooled down.

With melting of the blend and temperature raising to reach the set up values the torque started to decrease. After 5 min the temperature was set to increase from 160 to 190 °C.

This resulted in a sharp decrease of torque. The temperature levelled off to 190 °C after 10 min from the start of the test. The torque monotonically decreased when the temperature reached the steady value of 190 °C. After 25 min the torque decreased of about 85 % from its initial value registered at 10 min.

The torque reduction measured in our test were interpreted in terms of the polymer degradation during melt mixing. To assess the occurring microstructural changes, the major component of the blend (i.e. PLA) was extracted according to the procedure described in the experimental section after processing and further analyzed by SEC and DSC.

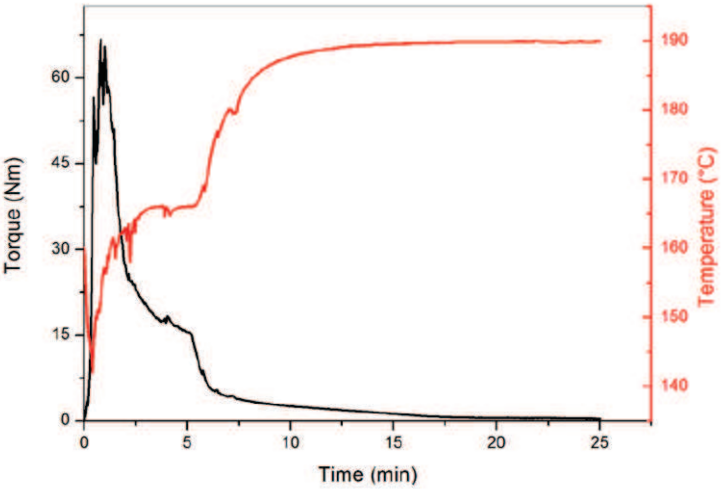


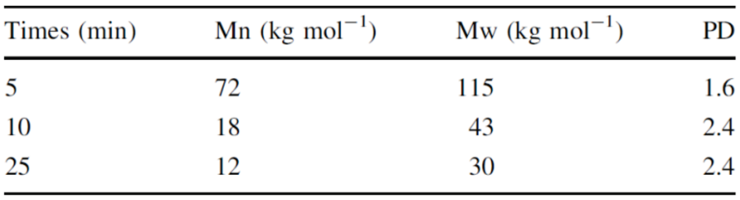
Figure 55-Torque versus time measurements data for all the test

The initial number average (Mn) and the weight average (Mw) molar masses of the PLA extracted from the virgin blend were 72 and 115 kg mol-1, respectively. These values dropped to lower values after 10 and 25 min of processing in the mixer chamber (Table 15). Mw dropped by 62 and 74 % after

10 and 25 min, respectively, while the polydispersity index increased from 1.6 to 2.4 after processing.

Le Marec et al. [6], having processed PLA in similar conditions, reported that Mw decreased by only 40 %, while the polydispersity index showed no significant change after processing for 30 min at 190 □C at 150 rpm. Yu et al. [7] reported that the polydispersity index increased up to 2 which is the asymptotic value in a random chain scission hypothesis. Pillin et al. [8] studied the recycling of PLA in repeated injection cycles up to 7 times. They reported Mw drops of about 30 % after 3 cycles and of 63 % after 7 cycles. The SEC data reported for our samples can be explained as a consequence of the presence of lignin reactive groups, like –OH, and –COOH, in the blend which can favor PLA degradation. As an example, the carboxyl group of lignin can favor acidolysis reactions in melt conditions. The degradation products of the melt processed blend are being investigated in order to clarify the role of reactive functional groups of the lignin; however, their complete characterization is out the scope of the present work.

Table 15- SEC data of PLA extracted from blends after different processing time



Times (min)	Mn (kg mol^{-1})	Mw (kg mol^{-1})	PD
5	72	115	1.6
10	18	43	2.4
25	12	30	2.4

In addition to the degradation of polymer chains the degradation of the ground softwood can influence the torque measurements. Migneault et at [9] reported the effect of different fiber length on torque measurement. In their study high density polyethylene was compounded with white birch pulp fibers with length varying from 0.481 to 0.196 mm. The study revealed that moving from long to short fibers cause a variation of stabilized torque from 16.3 to 13.6 Nm with a torque reduction of 17 %. Fiber reduction only cannot thus account for the high torque degradation registered in the sample presented here but it can contribute to the overall torque reduction.

DSC curves on PLA extracted from the processed blend confirmed the presence of microstructural changes for the PLA component after processing at 190 °C (Fig. 56). Table 16 presents the evolution of heat capacity of the PLA samples extracted from blends obtained after different processing times and the values of the different temperatures and enthalpies (Tg for glass transition temperature, Tc and DHc for crystallization temperature and enthalpy, Tm1, Tm2 and DHm for both melting temperatures and total melting enthalpy) in relation with the previously determined weight-average molar mass.

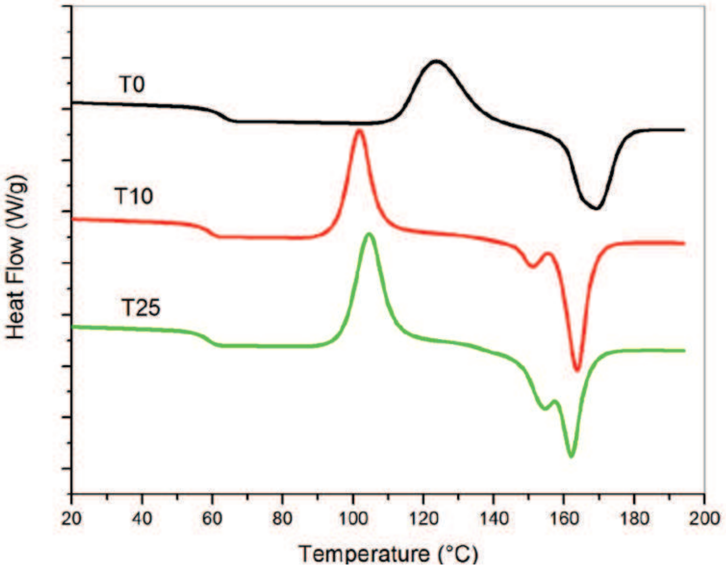


Figure 56- DSC curves for PLA extracted from the blend: as received (T0), after 10 min (T10) and 25 min (T25) in the batch mixer (scan run at 20 °C/min in nitrogen. 2nd heating reported)

Table 16- Transition temperature and enthalpies after different processing time for PLA extracted from the blends

Times (min)	Mw (kg mol^{-1})	Tg (°C)	T_c (°C)	ΔH_c (kJ/kg)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (kJ/kg)
0	115	63.2	123.5	55.1	–	169.3	53.8
10	43	59.4	101.7	60.0	151.0	163.7	63.0
25	30	58.9	104.6	64.0	154.5	162.0	64.7

It can be observed that glass transition is slightly reduced by processing, thus it drops from 63.2 °C, for PLA extracted from the virgin blend, to 59.4 and 58.9 °C for the blends processed for 10 and 25 min. Tc is also reduced from 123.5 to 101.7 and 104.6 °C for T10 and T25 samples, respectively. The overall melting enthalpies increased with increasing degradation. The melting behavior was more complicated for degraded samples since two melting peaks appeared. Le Marec et al. [6] found similar behavior that was explained in terms of the appearance of polymorphism due to molar mass decrease.

In order to assess the industrial validity of the blend its mechanical properties must stay as stable as possible along with the processing times. Therefore, the tensile modulus, ultimate tensile strength and strain to failure of the blend was measured as function of processing time.

Figure 57 summarizes the mechanical properties results. Ultimate tensile strength dropped from 29.75 to 4.85 MPa with a reduction of 84 % after 25 min. Tensile modulus dropped from 5.3 to 4.2 GPa with a reduction of 21 %. The strain to failure (e) decreased from 0.63 to 0.14 % with a reduction of 77 %. Pillin et al. [8], for unreinforced PLLA, reported decreases of the ultimate tensile strength, after 7 cycles, up to 64 % but no significant change in tensile modulus. Zenkiewicz et al. [10] reported reductions of the tensile strength after 10 extrusion cycles for neat PLA while tensile modulus did not vary significantly. The virgin blend characterized here showed significant reductions for all the mechanical properties measured with increasing processing time. This finding should be interpreted bearing in mind that the system analyzed is a blend of PLA with soft wood and lignin.

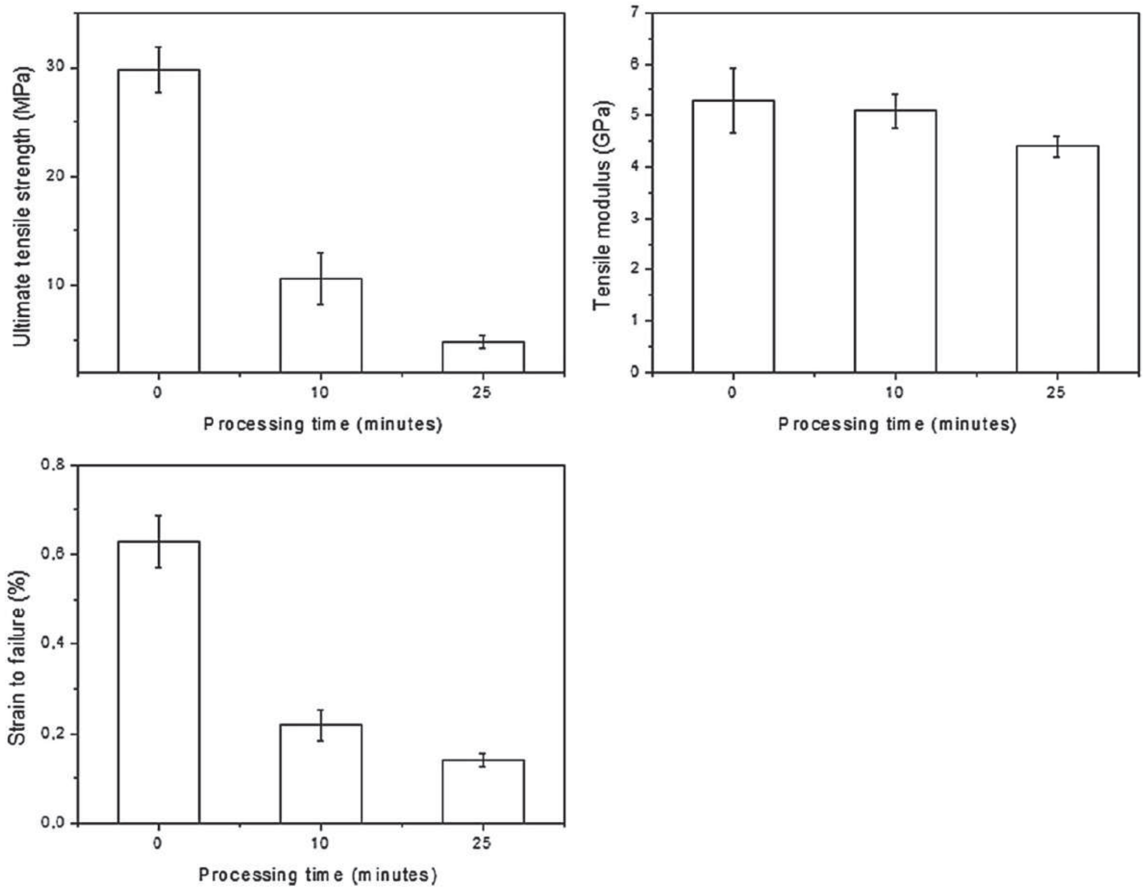


Figure 57- Tensile properties of the blends: as received (T0), after 10 min (T10) and 25 min (T25) in the batch mixer (error bars display the SD measured)

The mechanical behavior of virgin samples (T0) can be explained as a result of blending PLA with lignin and soft wood. Gordobil et al. [11] focused on PLA mixed with Kraft lignin and acetylated Kraft lignin. When lignin was added up to 10 or 20 wt% tensile strength and strain to failure dropped while tensile modulus increased for lignin content up to 10 wt%. Domenek et al. [12] found similar results using two commercial lignin grades. The tensile strength of the virgin blend fits with the values measured by Gordobil et al. that reported values between 35 and

15 MPa for 20 wt% of acetylated Kraft lignin and unmodified kraft lignin, respectively. However, the tensile modulus measured by Gordobil et al. [11] was lower (*3 GPa) than the modulus measured for the virgin blend (i.e. 5.2 GPa) analyzed here. This difference is explained by the reinforcement effect of the 15.4 wt% soft wood found in the LV1000.

The mechanical properties of the degraded samples indicated a severe reduction for all the tensile properties with increasing processing time. Le Duigou et al. [13] presented a study on a PLLA reinforced system analogous to the unreinforced matrix studied by Pillin et al. [8]. The system was reinforced with the addition of flax short fibers and the recycling after several injection steps was evaluated.

The results showed modulus reduction of 12 and 7.7 % for samples reinforced with 20 and 30 wt% of flax fibers, respectively. Their systems showed also smaller reduction of the tensile strength and of the strain at failure compared to the virgin blend studied here. Graupner et al. [14] in a recent paper showed similar trends for the tensile strength of cellulose reinforced PLA but no reduction in tensile modulus was discussed and the calorimetric properties did not change significantly due to reprocessing. The degradation of tensile properties for the virgin blend reported here is the result of the combination of two factors: the degrading effect of lignin on PLA and the reduction in cellulose fiber length from the 15.4 wt% soft wood. The two factors interact and contribute to the deterioration of the tensile properties of the virgin blend which showed higher degradation than those observed for neat and natural fiber reinforced PLA.

Wood like material from commercial sources was investigated.The composition of this product was unveiled showing the presence of PLA as a major component (75–77 wt%) while 15.4 wt% ground softwood and 5 wt% analysis allowed to shed more light on the thermal behavior observed by DSC analysis which presented a Tg of 61.3 °C (67.1 °C from DMA) and an endothermic peak at 171.0 °C.

The processing stability of the blend as a function of processing time at 190 □C was also studied. The decreasing torque measured from batch mixing experiment was interpreted in the context of the PLA degradation. The contribution of lignin reactive groups to PLA degradation and the degradation of soft wood were shown to be relevant leading to the appearance of double melting peaks and the tensile properties reductions. The double melting peak behavior followed the trend observed by other researches for neat PLA even if the molar mass decays were much higher than those reported for neat PLA. The presence of lignin led to tensile properties decays which are higher than those observed for neat PLA and reinforced PLA as reported in open literature. These findings are of interest for those involved with processing or recycling of PLA/ lignin/soft wood blends.

5.5.2 Polylactide/lignin blends

The effect of processing temperature on lignin is analyzed by thermal desorption–gas chromatography/mass spectrometry first. The effect of processing conditions on the chemical structure of the PLA blended with the lignin is then studied by torque rheometry and SEC analysis.

The effect of processing conditions on the mechanicalproperties for all the blends is presented and discussed on the basis of the findings from the previous analyses. Finally, the thermal stability is studied by thermal gravimetric analysis.

The mainly identified thermal desorption product from lignin consists of a variety of simple to more complex substituted phenol and benzene, all of which represent the three main phenylpropene monomers constitutive of its structure as reported in the literature [15, 16]. The spectra obtained at 170, 180 and 190 °C (Fig. 58) show that the increase in temperature does not produce spectra’s modification in terms of the type of the products released. Most products were identified in comparison with mass spectra Nist, Wiley and Florence and Fragrance library, in the case

where the matching is below 90%, the compound is considered as ‘‘non-identified’’ (Table 17). The major component of identified phenol is Ethanone-

1-(4-hydroxy-3,5-dimethoxyphenyl) with a retention time of 18.4 min. In addition, the presence of carboxylic acids is also observed with the presence of hexadecanoic acid with a retention time of 20.8 min.

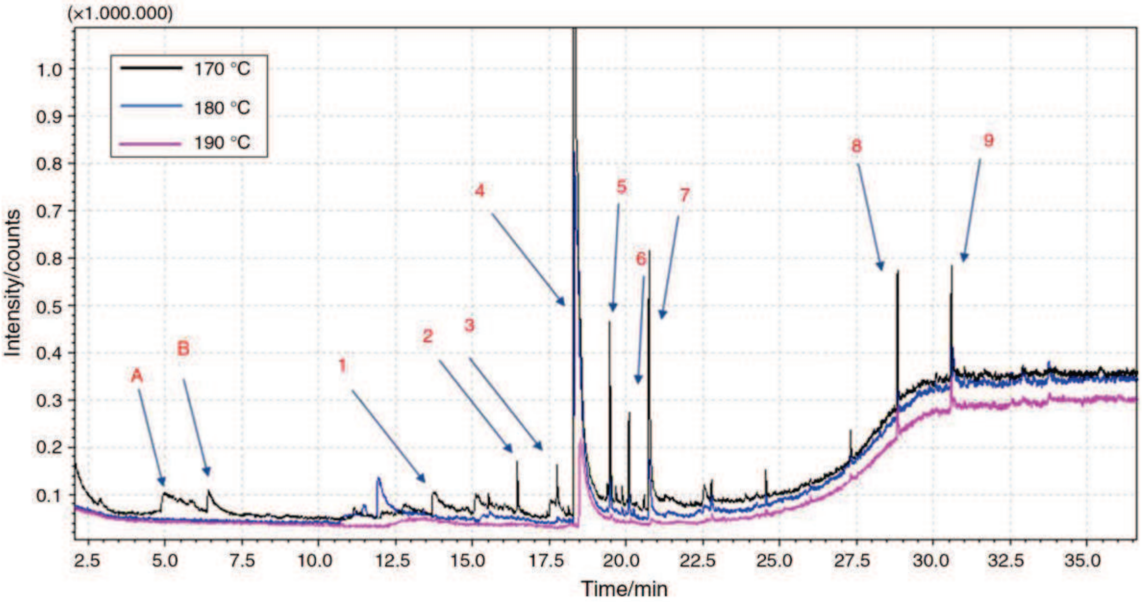
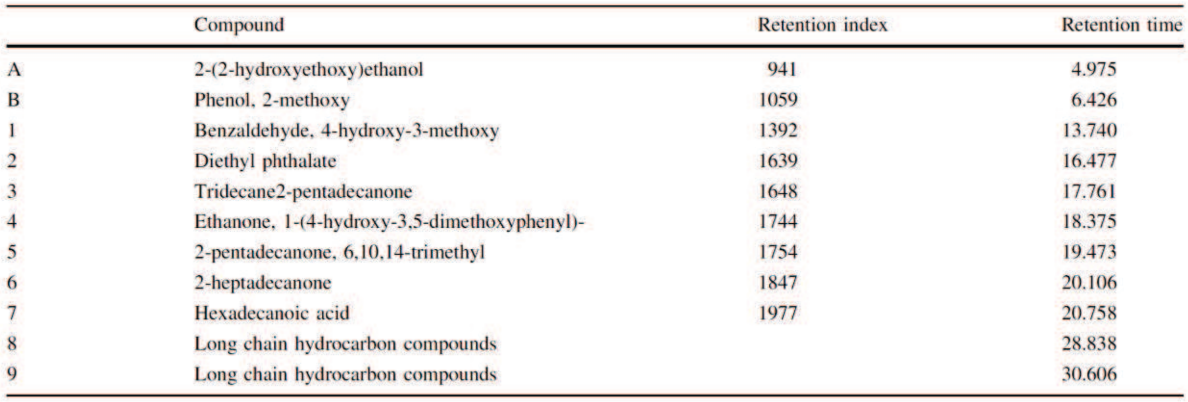


Figure 58- Thermal desorption–gas chromatography/mass spectra for lignin at 170, 180 and 190 °C

Table 17 Compounds released from thermal desorption tests



	Compound	Retention index	Retention time
A	2-(2-hydroxyethoxy)ethanol	941	4.975
B	Phenol, 2-methoxy	1059	6.426
1	Benzaldehyde, 4-hydroxy-3-methoxy	1392	13.740
2	Diethyl phthalate	1639	16.477
3	Tridecane2-pentadecanone	1648	17.761
4	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	1744	18.375
5	2-pentadecanone, 6,10,14-trimethyl	1754	19.473
6	2-heptadecanone	1847	20.106
7	Hexadecanoic acid	1977	20.758
8	Long chain hydrocarbon compounds		28.838
9	Long chain hydrocarbon compounds		30.606

In Fig. 59 are shown, as example, two mass spectra (experimental, a and b, and from the library a0 and b0) of the two products reported above. However, it must be noted that varying the testing temperature from 170 °C to 190 °C the products release is faster.

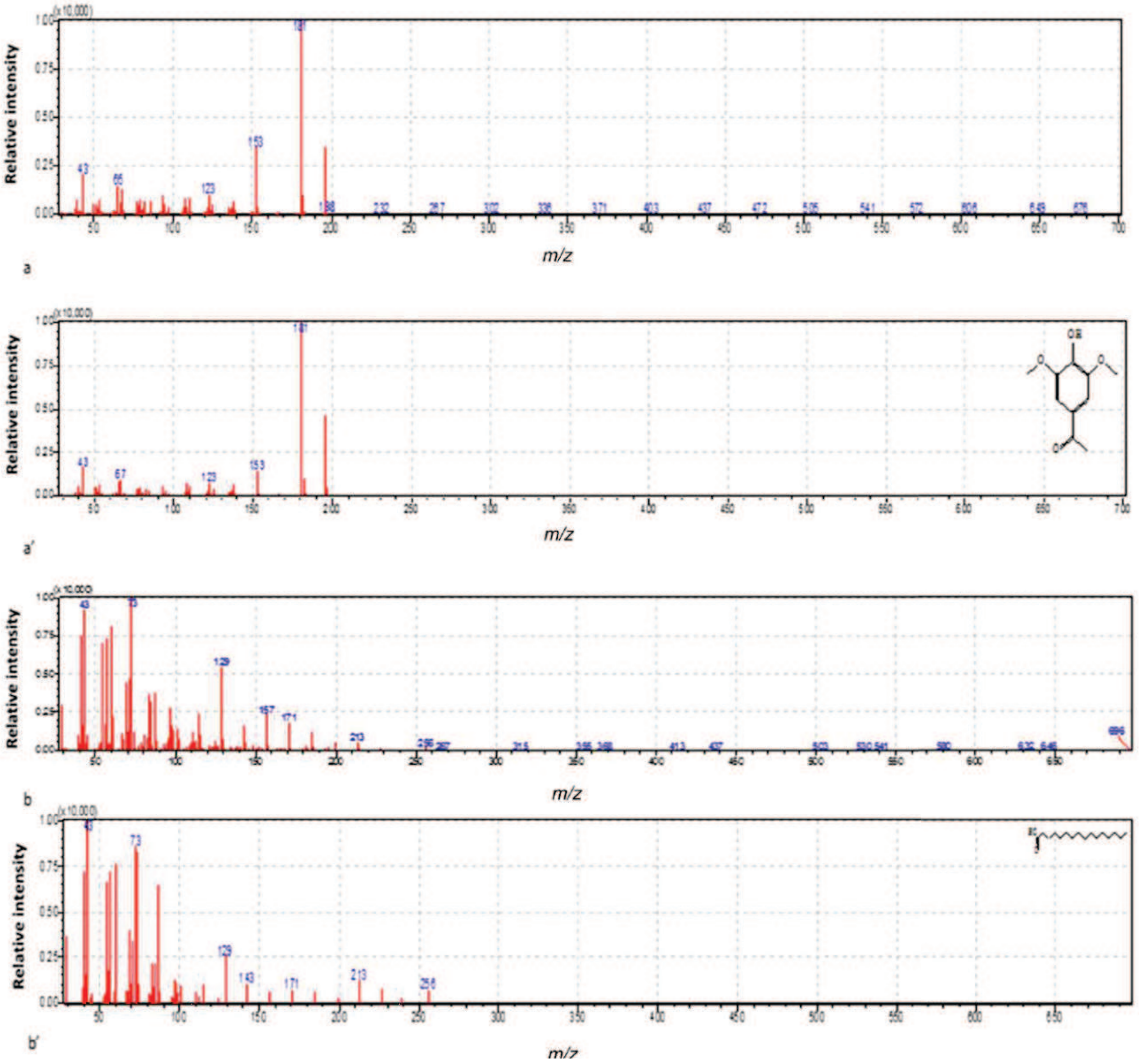


Figure 59- Mass spectra comparison for experimental curve (a and b) and from the library (a0 and b0)

The processing stability of the blends was first studied monitoring the torque in the batch mixer. The typical torque curves obtained for LV and PLA at 190 °C are showed in Fig. 60. The torque showed a sudden increase in the first minute due to polymer pellets loading and melting in the chamber which, because of polymer loading, cooled down in the batch mixer. With melting of the blend and temperature raising to reach the setup values the torque started to decrease. After 5 min, the temperature was set to increase from 160 to 190 °C. This resulted in a sharp decrease in torque. The temperature levelled off to 190 °C after 10 min from the start of the test. The torque monotonically decreased when the temperature reached the steady value of 190 °C. After 25 min, the torque decreased from its initial value registered at 10 min.

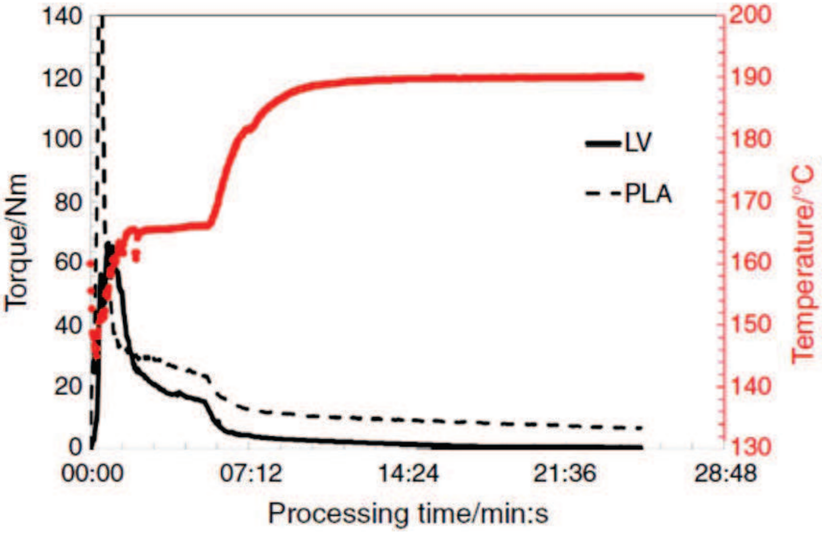


Figure 60- Torque versus time measurements data for LV and neat PLA at 190 °C

In order to make direct comparisons of the torque decrease for different blends or different processing temperatures, normalized torque was calculated. The normalized torque is obtained by dividing the measured torque for the torque value measured at 10 min from the start of the test. The normalized torque vs time curves for the test reported in Fig. 60 is displayed in Fig. 61. The torque degradation is different for PLA and LV. After 25 min, the torque decreased of about 85 and 37% from its initial value registered at 10 min for LV and PLA, respectively. The higher degradation for LV was explained as the result of the degradation of its major constituent (i.e., PLA) due to the effect of the lignin reactive groups and of the degradation of the softwood [17].

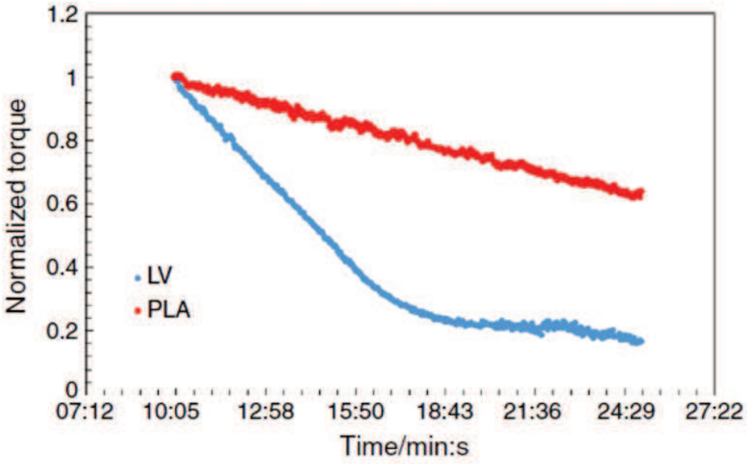


Figure 61- Normalized torque versus time for LV and neat PLA at 190 °C

The interpretation of the results for the LV blend is complicated by the presence of multiple constituents in theblend. In order to clarify the effect of lignin, blends of PLA and lignin were prepared. Blends with different amounts of lignin were processed in the batch mixer monitoring the torque during all the tests. The results, in terms of the normalized torque, are shown in Fig. 62. After 25 min, the torque decreased of about 68 and 83% from its initial value registered at 10 min for the blends with 10 and 25 mass% of lignin, respectively. This result shows that the lignin accelerates the PLA degradation. This finding is a consequence of the reactive groups of lignin but can also be ascribed to the by-products released from lignin at 190 °C which were identified by the thermal desorption analysis. In addition, it can be observed that the torque reduction for the sample with 25 mass% of lignin is in the same range of those found on the LV.

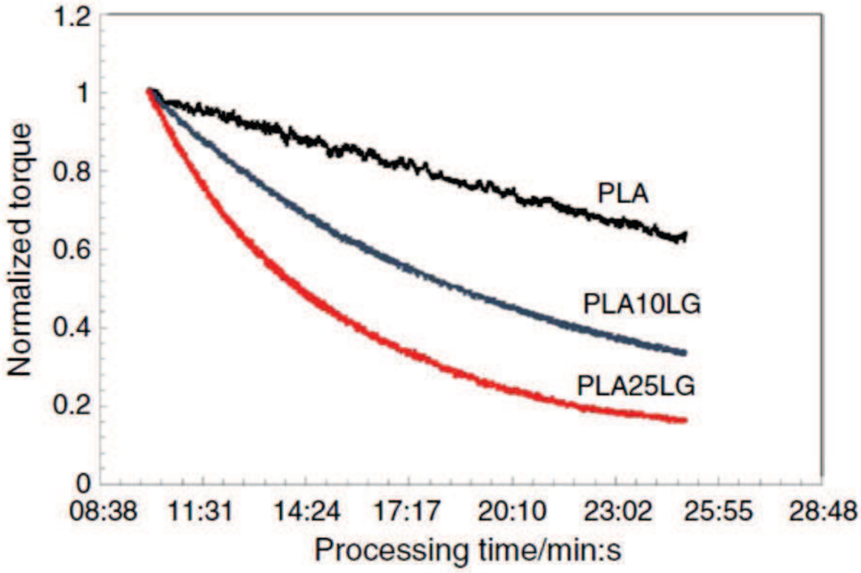


Figure 62- Normalized torque versus time for PLA/lignin blends at 190 °C

The effect of decreasing the processing temperature was also investigated by processing the blends at 170 °C. The effects of the lower processing temperature are shown in Figs. 63 and 64 for LV and the blend of PLA with lignin, respectively. The torque decrease for LV after 25 min varied from 84 to 45% reducing the processing temperature from 190 to 170 °C (Fig. 62). The torque decrease was reduced by 20% only for the blend with 10 mass% of lignin. The blend with 25 mass% of lignin showed a torque reduction of 57% which is higher than the value found for LV at the same processing temperature (i.e., 170 °C) but lower than the 83% found for the blend at 190 °C (Fig. 64). This result is a consequence of the higher content of lignin compared to the commercial LV. On the one hand, reducing the processing temperature increased the processing stability over the LV but, for high lignin content (i.e., 25 mass%), the positive effect was canceled by the presence of the higher concentration of reactive groups.

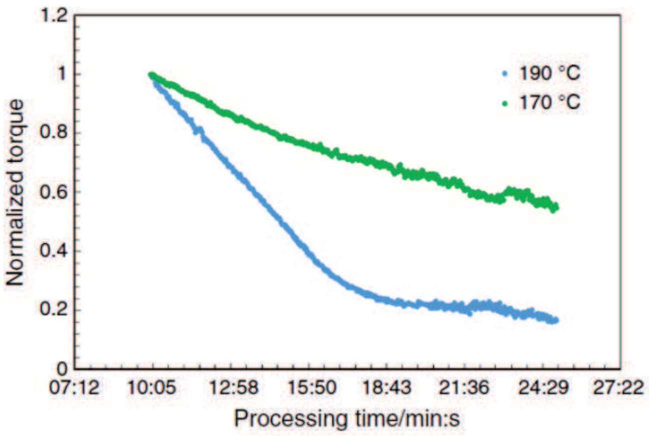


Figure 63- Normalized torque versus time for the LV processed at 170 and 190 °C

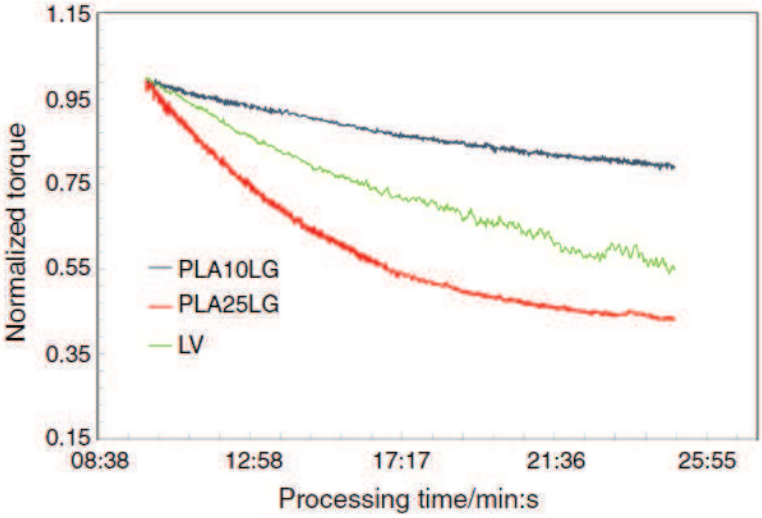


Figure 64- Normalized torque versus time for the PLA/lignin blends at 170 °C

The torque reduction measured in our test was interpreted in terms of the polymer degradation during melt mixing as shown in previous works [17, 18]. To assess the occurring microstructural changes, the major component of the blend (i.e., PLA) was extracted according to the procedure described in Experimental section after processing and further analyzed by SEC.

The initial average (Mw) molar masses of the PLA extracted from the LV sample was 115 kg mol-1, respectively. This value dropped to lower values after 10 and 25 min of processing in the mixer chamber at 190 or

170 °C (Fig. 65). Mw dropped by 62 and 74% after 10 and 25 min when processing temperature was set to 190 °C, respectively. When the processing temperature was lowered to 170 °C, the Mw dropped by 20 and 27% after 10 and 25 min.

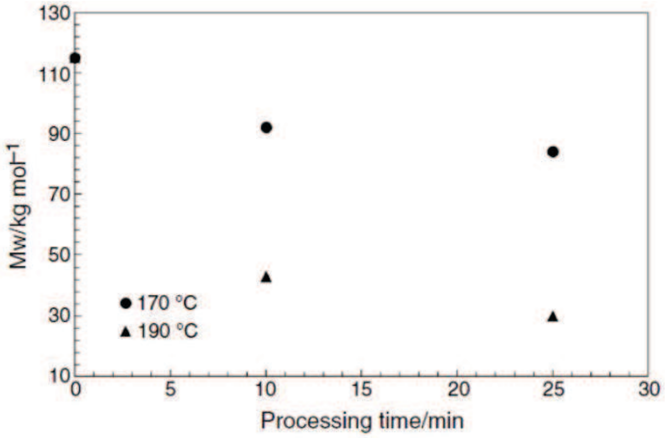


Figure 65- Average molecular mass for the PLA extracted from the LV before and after processing

The average molar mass for the PLA/lignin blends is reported in Fig. 66. The neat PLA showed only 4 and 8% Mw reduction for processing at 190 °C after 10 and 25 min,respectively. No data were calculated at 170 °C because,due to the high viscosity of the neat PLA, the polymer could not be processed at 170 °C. The addition of lignin led to higher average molar mass decreases compared to neat PLA. For the processing temperature of 190 °C increasing the lignin content from 10 to 25 mass% resulted in the Mw decreases from 39 to 57% after 25 min while, when the processing temperature was lowered to 170 °C, the decreases varied from 15 to 37%. These values were lower than those measured for the LV blend with the exception of the sample with 25 mass% of lignin processed at 170 °C for 25 min. This result confirms the findings of the torque rheometry.

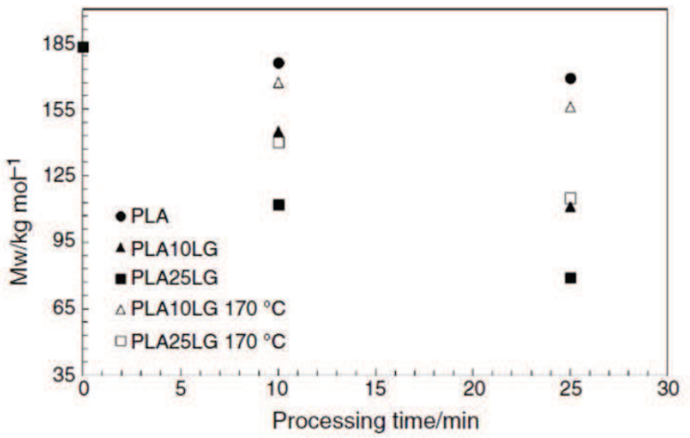


Figure 66- Average molecular mass for the PLA extracted from the PLA/ lignin blends before and after processing

The tensile modulus, ultimate tensile strength and strain to failure of the blends were measured as function of processing temperatures and times. This information is crucial to determine the processing conditions to have reliable mechanical properties and to evaluate the recyclability of the blends studied here. Fig.67 displays the ultimate tensile strength (Fig. 67a) and the tensile modulus (Fig. 67b) for the commercial LV blend and for the blends with different amount of lignin as function of the processing time for the two mixing temperatures tested. The data at 0 min refer to the as-received blend with no further processing. The LV blend, when processed at 190 °C, showed decreasing mechanical properties for increasing processing times. The LV blend processed at 170 °C showed more stable properties with increasing processing times. The ultimate tensile strength for the LV blend processed at 170 °C varied from 10.64 to 13.19 MPa processing the blend from 10 to 25 min. The tensile modulus varied from 5.20 to 5.30 GPa which indicates that, for processing temperature of 170 °C, no degradation in modulus occurred compared to the as received blend (5.30 GPa).

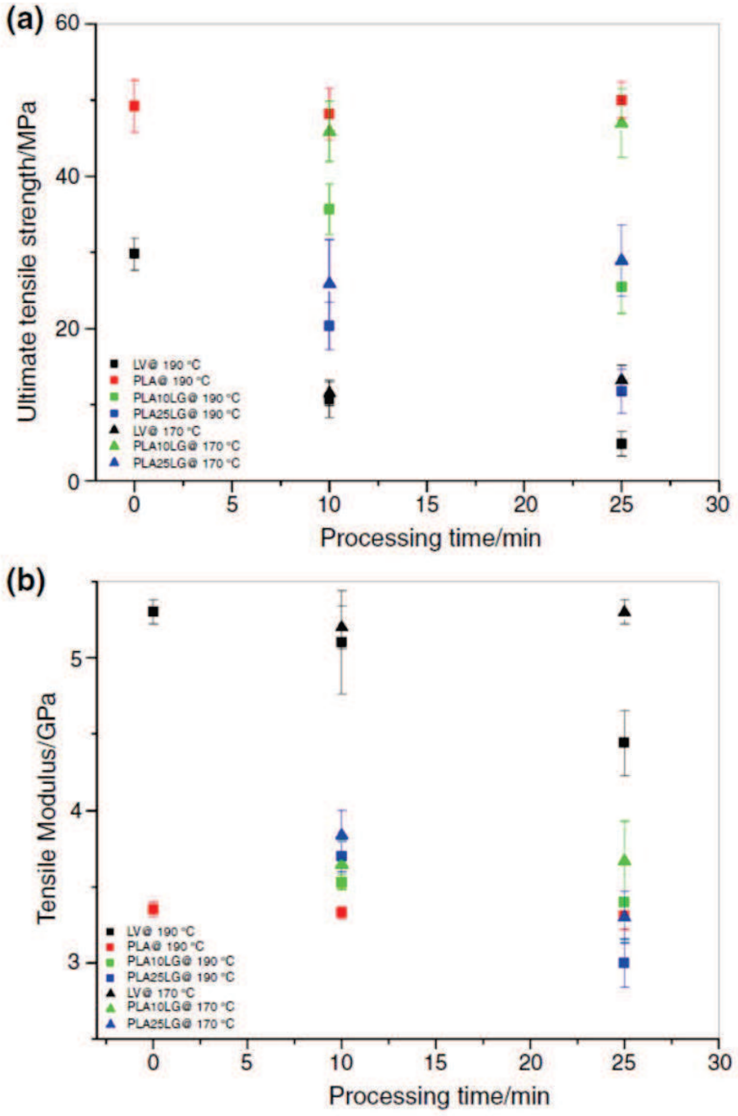


Figure 67- Ultimate tensile strength (a) and tensile modulus (b) for LV and PLA/lignin blends

The ultimate tensile strength and the tensile modulus of The unmodified PLA showed only small variation after processing at 190 °C both at 10 and at 25 min. The addition of 10 and 25 mass% of lignin caused severe degradation in tensile strength for the samples processed at 190 °C for 25 min. The tensile modulus showed also a decreasing trend with increasing processing times. However, the tensile modulus for the blends showed similar or higher values compared to the unmodified blends due to the reinforcement effect of the lignin.

In the worst case, i.e., the sample at 25 mass% of lignin processed for 25 min at 190 °C, the tensile strength dropped from 49.96 MPa, for the unmodified PLA processed with the same cycle, to 11.75 MPa of the lignin-modified sample. Reducing the lignin content to 10 mass% limited the tensile strength drop for processing at 190 °C after 25 min to 25.45 MPa. However, it is only processing the blend at 170 °C and with the limitation of a low lignin content (i.e., 10 mass%) that the PLA/lignin blends displayed very small variation in tensile strength while keeping a reinforcement effect on the tensile modulus.

The mechanical properties of the degraded LV and PLA/lignin samples indicated that the reduction for all the tensile properties can be mitigated by reducing the processing temperature from 190 to 170 °C. The processing stability of the LV blends is the combination of two factors: the degrading effect of lignin on PLA; the reduction in cellulose fiber length from the 15.4 mass% softwood. The reduction in the processing temperature from 190 to 170 °C limits the thermal degradation of lignin lowering the release of lignin by-products which, in turn, degraded less the PLA chains of the blend. This result is supported by the analysis of the mechanical properties for the PLA loaded with 10 mass% of lignin when processed at 170 °C.

The thermal behavior of our compounds was studied by TGand DTA experiments in the temperature range 35–600 °C, in static air atmosphere. The TG/DTA curves (Fig. 68a–c) did not show any mass loss up to 250 °

C, after which composites lost mass in two degradation steps.

For all studied compounds were observed a first degradation stage, in every case included in the 250–350 °C temperature range, associated with the most part of mass loss (80–90%), immediately followed by another one at higher temperature without char formation.

The initial temperatures of decomposition (Ti), which are a measure of thermal stability and can be obtained by the experimental curves as the intersection between the starting mass line and the maximum gradient tangent to theTG curve [19], were determined and used for the comparisons among the various compounds investigated (Table 18).

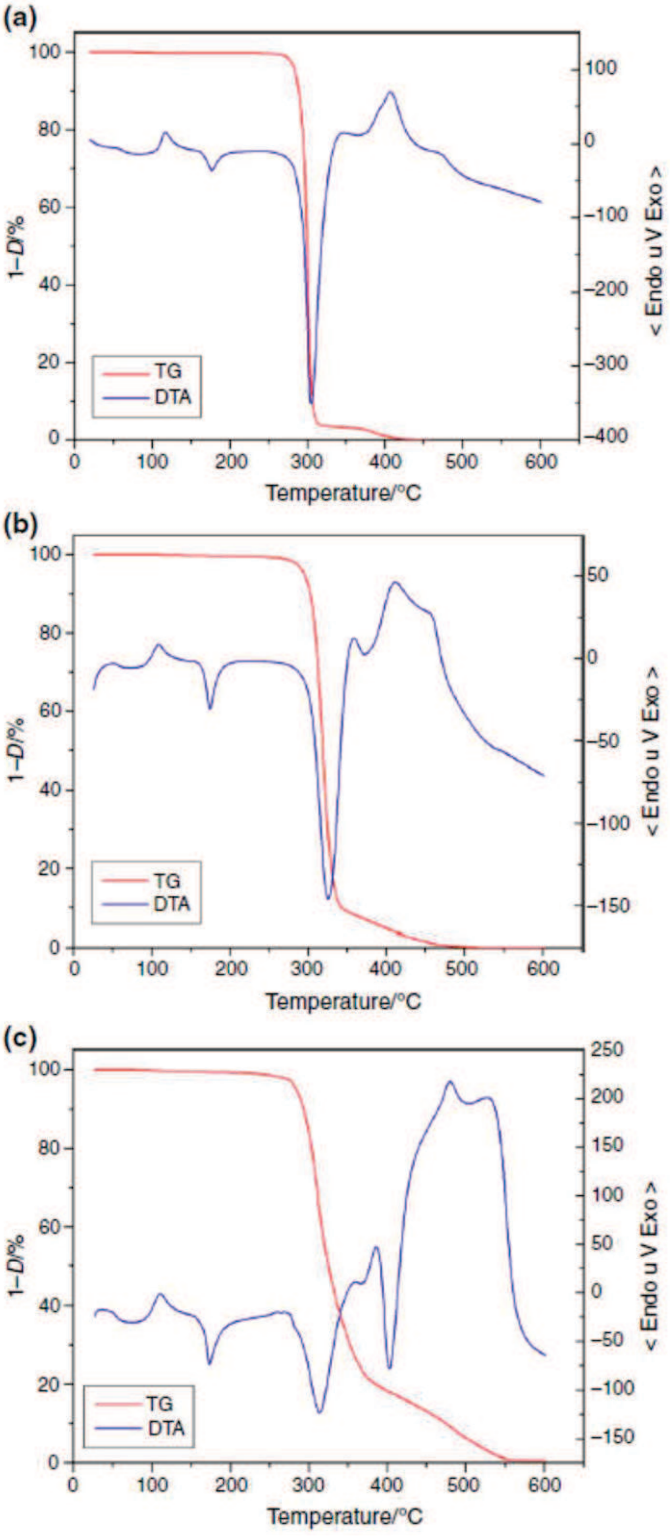
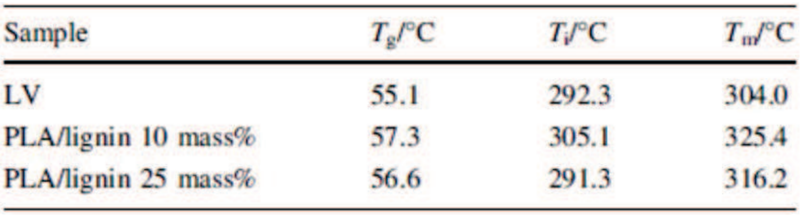


Figure 68- G/DTA curves for LV (a), PLA/lignin 10 mass% blend (b) and PLA/lignin 25 mass% blend (c)

Table 18- Glass transition temperatures (Tg), initial temperatures of decomposition (Ti) and temperature of maximum mass loss (Tm) values for LV (a), PLA/lignin 10 mass% blend (b) and PLA/lignin 25 mass% blend



Sample	T_g/°C	T_i/°C	T_m/°C
LV	55.1	292.3	304.0
PLA/lignin 10 mass%	57.3	305.1	325.4
PLA/lignin 25 mass%	56.6	291.3	316.2

The introduction of 10% of lignin in polymer composite lead to an increase in both Ti and temperature of maximum mass loss (Tm) values (Fig. 69), while a furtheradding of lignin up to 25% lowers the heat resistance (which depends on Ti), but, also, the degradation rate as confirmed by the differences (Tm - Ti), which can be roughly considered a measure of the degradation rate. The DTA analyses, apart confirm the exothermic decomposition above 400 °C and a sharp endothermic peak corresponding to the main stage of degradation, presented the characteristic thermal profile of PLA [20–22]. DTA curves of the composites (Fig. 68a–c) show a glass transition shortly before 60 □C, which remains substantially unchanged by passing from the net sample to those with addition of lignin (Tab. 18), and an exothermal peak whose onset temperature oscillates in the neighborhood of 100 °C and the melting peak that falls at about 160 °C.

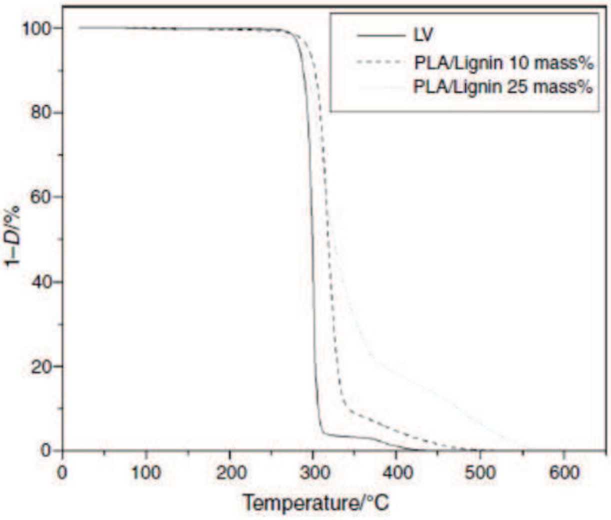


Figure 69- TG curves of LV, PLA/lignin 10 mass% blend and PLA/ lignin 25 mass% blend

Wood-like material from a commercial source was further investigated and its behavior compared to a blend prepared by melt mixing. The presence of lignin in both the systems showed to have a profound effect on the processing stability of the systems. The commercial LV blend showed the worst processing stability at 190 °C as the combined effect of lignin and softwood on PLA degradation. The effect of lignin is twofold: the effect of lignin reactive groups which break the PLA chains; the by-products released by the thermal degradation of lignin at the processing temperature which release molecular substances which can break the PLA chains.

The degradation trends observed on the LV system were further unveiled by the study of the PLA/lignin blends. The blends containing lignin only and not ground softwood, as in LV, showed good processing stability at 170 °C. This finding was explained by the improved stability of lignin at 170 °C, which had minor effects of PLA degradation of the PLA/lignin blends. These findings are of interest for those involved with processing or recycling of PLA/lignin blends.

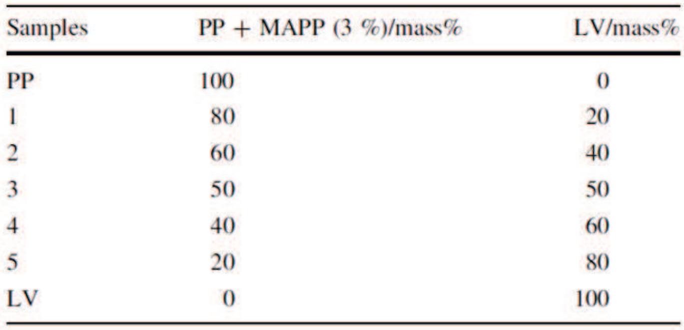
5.5.3 Lignin-based polypropylene blends

Polypropylene (PP), due to its chemical stability, is considered one of the main responsible of the increasing amount of plastic wastes on earth. To overcome this problem and to reduce the dependence of oil feedstocks, the use of lignocellulosics as fillers or reinforcements in thermoplastic materials has been increasing enormously in the last decades. The Liquid Wood LV1000 was used to prepare, by mechanical mixing followed by thermal extrusion, blends of various PP/Liquid Wood ratios. The preparation of these blends followed the study of the fully biobased blends presented in the previous paragraph and it is complementary. The industrial need for such study is due to the lower cost of PP compared to PLA and to its higher thermal stability. The PP based blends are obviously characterized by a lower biocarbon content. However, we considered interesting to perform such study as the commercial exploitation could be faster for such blends thus increasing the acceptance of lignin as a viable natural filler. Most of the preparation of these blends was performed at the Technical University of Clausthal (Germany).

Blends of various PP/LV ratios (Table 19) were prepared by mechanical mixing followed by thermal extrusion using a Berstorff ZE25Ax40D extruder. The sequence of compounding was as following: PP and MAPP were previously mixed (3 % of MAPP) and then fed through an input hopper; finally, the LV was inserted from the extruder opening side. The temperature profile of the extruder was 220–210–200–195–190–195–200 °C from input to output zones. The blends were pelletized from the extruded filament. Compounded pellets were dried (24 h at 30 °C under

vacuum) before injection moulding which was carried out using an injection moulding press, Arburg, with a temperature profile of 185–190–195–200 °C in a room temperature mould at maximum clamping force of 600 kN.

Table 19 Blends formulations



Samples	PP + MAPP (3 %)/mass%	LV/mass%
PP	100	0
1	80	20
2	60	40
3	50	50
4	40	60
5	20	80
LV	0	100

All samples were at first calorimetrically characterized by heating from -20 °C up to melting and their DSC curves are reported in Fig. 1, whilst data of the characteristic temperatures and enthalpies are reported in Table 20. As shown in Fig. 1, polypropylene evidenced the classical DSC trace which finishes with the melting at Tonset = 150.9 °C [23]. More interesting are the DSC curves of the blends (Fig. 70) which, besides the melting that shift towards higher temperatures on increasing the LV content, show a glass transition shortly before 60 °C and an exothermal peak whose onset temperature oscillates in the neighbourhood of 90 °C. Both of these phenomena become more evident with increasing the LV content in blends and can be attributed, in our opinion, to polylactic acid (PLA) (probably added to improve the workability of Liquid Wood). The presence of PLA, which was already confirmed by the previous analyses, is unequivocally confirmed by the melting peak observed in the pure sample of LV (Fig. 70) that falls in the melting range, well known in the literature [24–26], of pure PLA.

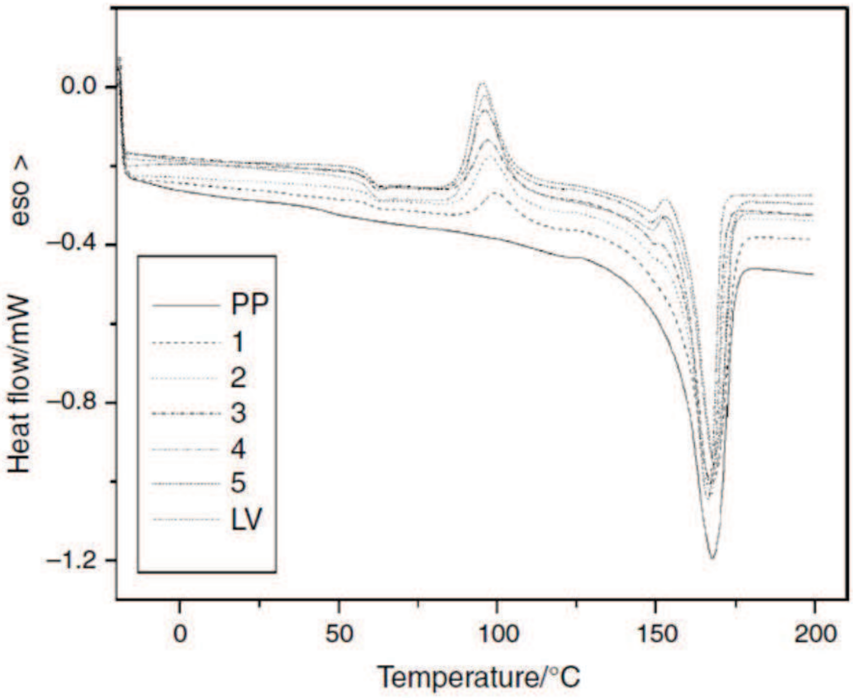
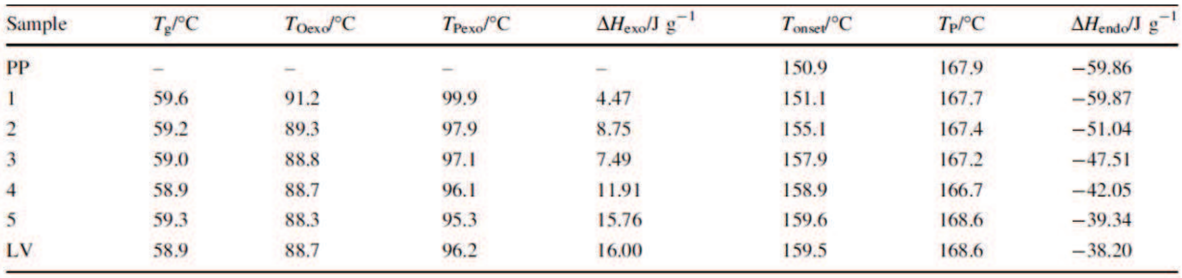


Figure 70- DSC curves, at 10 °C min-1, of polypropylene (PP), samples 1, 2, 3, 4, 5 and LV

Table 20- Glass transition temperature (Tg), onset (TOexo) and peak (TPexo) temperature and enthalpy (DHexo) of the exothermal transition, onset (Tonset)

and peak (TP) temperature and enthalpy (DHendo) of melting of the studied compounds



Sample	T_g/°C	T_{Oexo}/°C	T_{Pexo}/°C	ΔH_{exo}/J g^{-1}	T_{onset}/°C	T_P/°C	ΔH_{endo}/J g^{-1}
PP	–	–	–	–	150.9	167.9	−59.86
1	59.6	91.2	99.9	4.47	151.1	167.7	−59.87
2	59.2	89.3	97.9	8.75	155.1	167.4	−51.04
3	59.0	88.8	97.1	7.49	157.9	167.2	−47.51
4	58.9	88.7	96.1	11.91	158.9	166.7	−42.05
5	59.3	88.3	95.3	15.76	159.6	168.6	−39.34
LV	58.9	88.7	96.2	16.00	159.5	168.6	−38.20

By a careful observation of the DSC curves of samples 2–5, one can also observe the characteristic glass transition of lignin [27] that resulted in partially overlaps to the beginning of the melting of PP and PLA but that

becomes more and more evident with increasing content of LV in blends. Analysing the data in Table 20, one can observe how the melting temperature of the studied compounds grows by passing from pristine polypropylene to the blends at higher content of LV, due to the presence of PLA on considering that the maximum Tonset value was found for pure LV.

The scanning electron microscopy (SEM) micrographs of the tensile fractured surface for the LV sample is shown in Fig. 71a. The presence of spherical particles (*1–3 lm) and fibrous material dispersed in a PLA matrix is clearly showed. This result confirms the presence of soft wood as reported in the previous paragraphs. The spherical particles are lignin particles. In previous reports, focused on PLA/lignin blends, lignin particles were dispersed in PLA matrix showing similar morphologies [28, 29]. Figure 71b shows some degree of particle debonding from the matrix, which is a sign of a non-optimized adhesion between PLA and lignin.

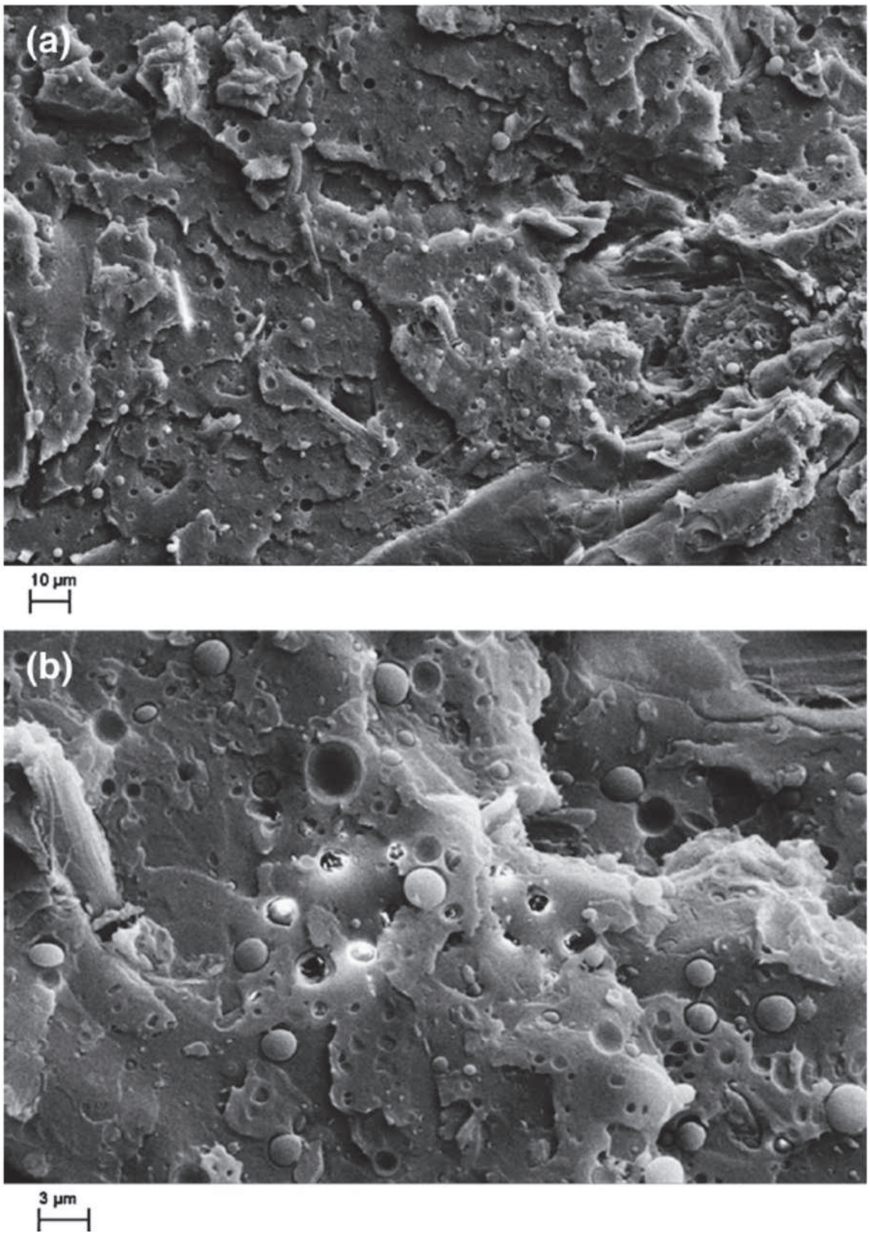


Figure 71- SEM of LV

The degradation of the studied compounds was thus carried out into a thermobalance in the scanning mode in order to determine two characteristic parameters of thermal degradation, namely temperature at 5 % mass loss (T5 %) and solid residue at 800 °C. The degradation TG curves of PP, LV and their blends are reported in Fig.72, whilst T5 % and residue values are reported in Table 21. The temperature at 5 % mass loss was chosen to evaluate the resistance to thermal degradation because it is, in our opinion, more reliable than initial decomposition temperature (Ti), whose determination is largely affected by the slope of descending piece of TG curve [30, 31], especially when, as in this case, it occurs in two consecutive degradation steps [32]. In the investigated temperature range (25–800 □C), polypropylene and Liquid Wood degraded in one single sharp step whilst their blends have shown two consecutive stages, whose intensity, clearly showed by the DTG curves as reported in Fig. 73, increases with their respective presence in the blend. The T5 % values of the 1–5 samples (Table 21) were largely higher than that of LV and, as shown in Fig. 74, increase exponentially on increasing the PP content.

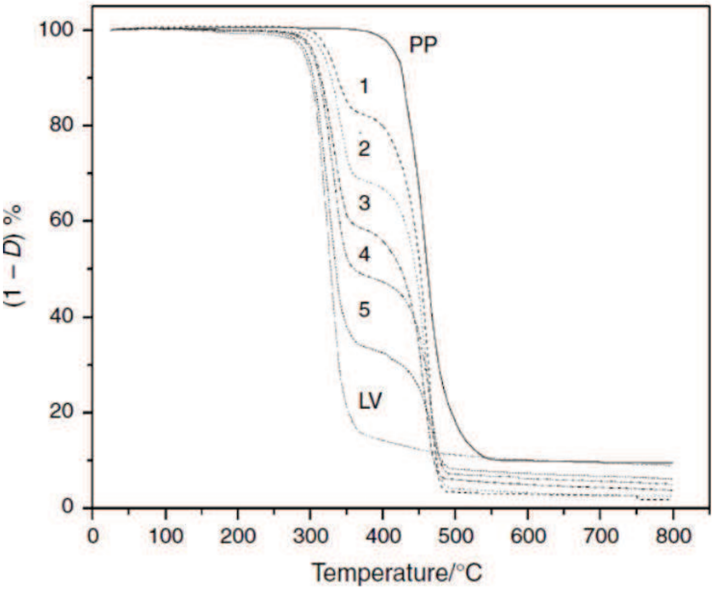
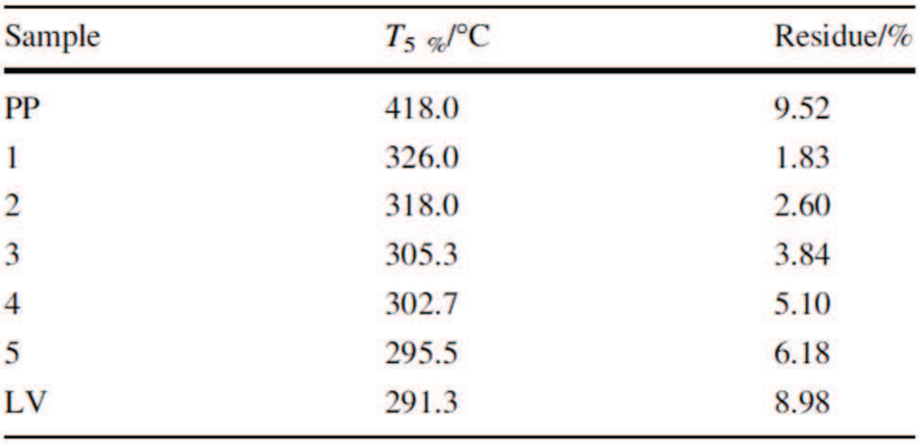


Figure 72- TG degradation curves, at 10 °C min^{-1}, of polypropylene (PP), sample 1, 2, 3, 4, 5 and LV

Table 21- Temperatures at 5 % mass loss (T5 %) and residue % at 800 _C of the studied compounds



Sample	$T_{5\ \%}$/°C	Residue/%
PP	418.0	9.52
1	326.0	1.83
2	318.0	2.60
3	305.3	3.84
4	302.7	5.10
5	295.5	6.18
LV	291.3	8.98

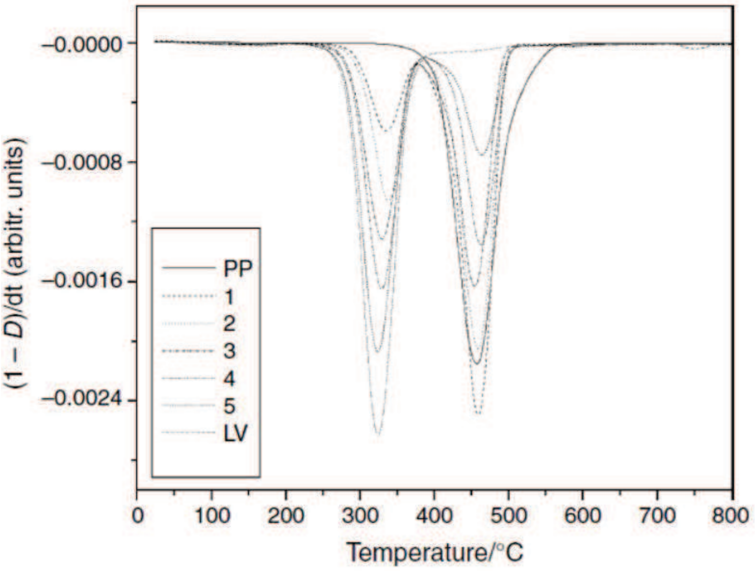


Figure 73- DTG degradation curves, at 10 °C min^{-1}, of polypropylene (PP), samples 1, 2, 3, 4, 5 and LV

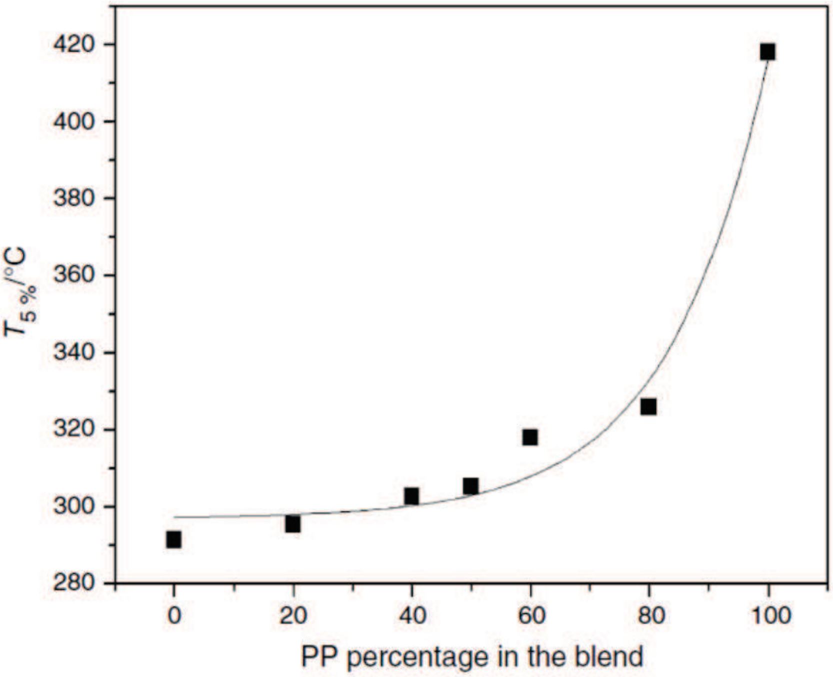


Figure 74- Temperature at 5 % mass loss (T5 %) of various samples as function of the polypropylene (PP) content in the blend

For all compounds, the presence of a stable residue at 800 °C was observed and the quantitative data are reported in Table 21 together with T5 % values. It is worth noting that, differently than PP and LV, whose residues lie around 10 %, all blends showed low values of residues that

increase in increasing the LV content (Fig. 75). These results clearly mean that the blending of PP with LV decreases the resistance to the thermal degradation of pristine polymer.

The fibrous material, which resembles the cross section of natural fibres [33], is clearly displayed by the SEM analysis of the polished cross section (Fig. 76). Sahoo et al. [34] evidenced the multicomponent nature of the LV100 grade demonstrating the presence of ground plant fibres like hemp, flax and wood in the lignin-based polymer composites used. This result confirms the presence of softwood fibres revealed by the chemical analysis showed before.

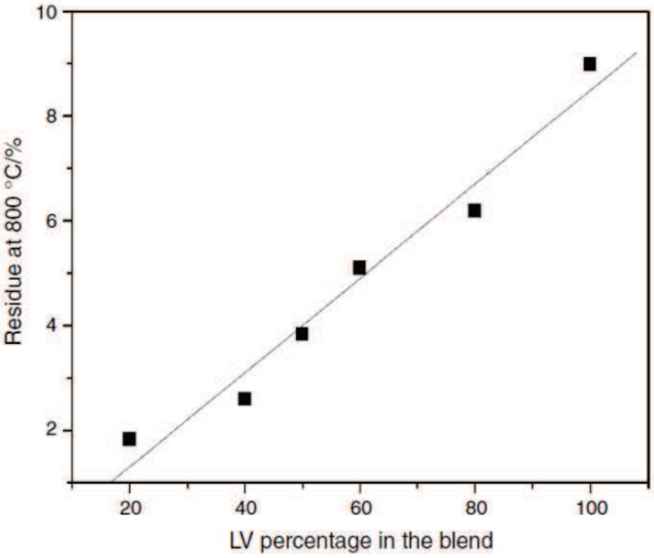


Figure 75- Residue % obtained at 800 °C as function of the LV content in the blend

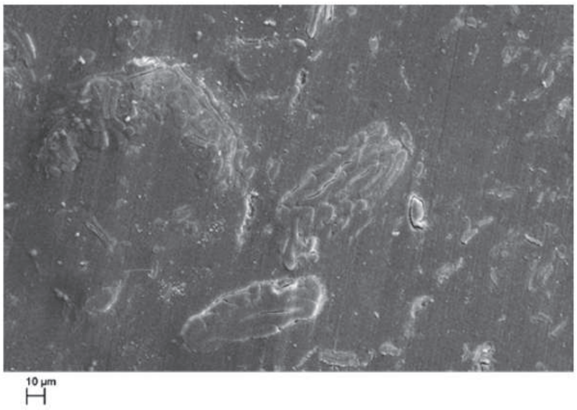


Figure 76- SEM detail of the surface of the LV

The tensile testing results are summarized in Fig. 77. Tensile strength and tensile modulus increased with increasing percentages of Liquid Wood. The tensile strength raised from 28.4 MPa, for the unmodified PP, to 44.7 MPa adding 80 mass% of LV, while the tensile modulus varied from 849 MPa to 3520 GPa for the same blends. Toriz et al. [35] showed different trends for PP/lignin blends with the tensile strength decreasing monotonically with lignin content and the tensile modulus increasing up to 30 mass% and then decreasing for higher lignin content. The explanation of the different trends found for our blends is twofold: PLA is present in the Liquid Wood mixture as shown by the thermal and microscopic characterization reported above; MAPP and lignin itself can interact to enhance the interfacial adhesion of the blends components. As reported by Reddy et al. [36] and Choudhary et al. [37], PP/PLA blends can show enhanced mechanical properties, despite the incompatibility of the pure polymers, when proper compatibilizers, like MAPP, are used. The ester groups of PLA can interact with lignin, and the anhydride groups of MAPP can react with cellulose.

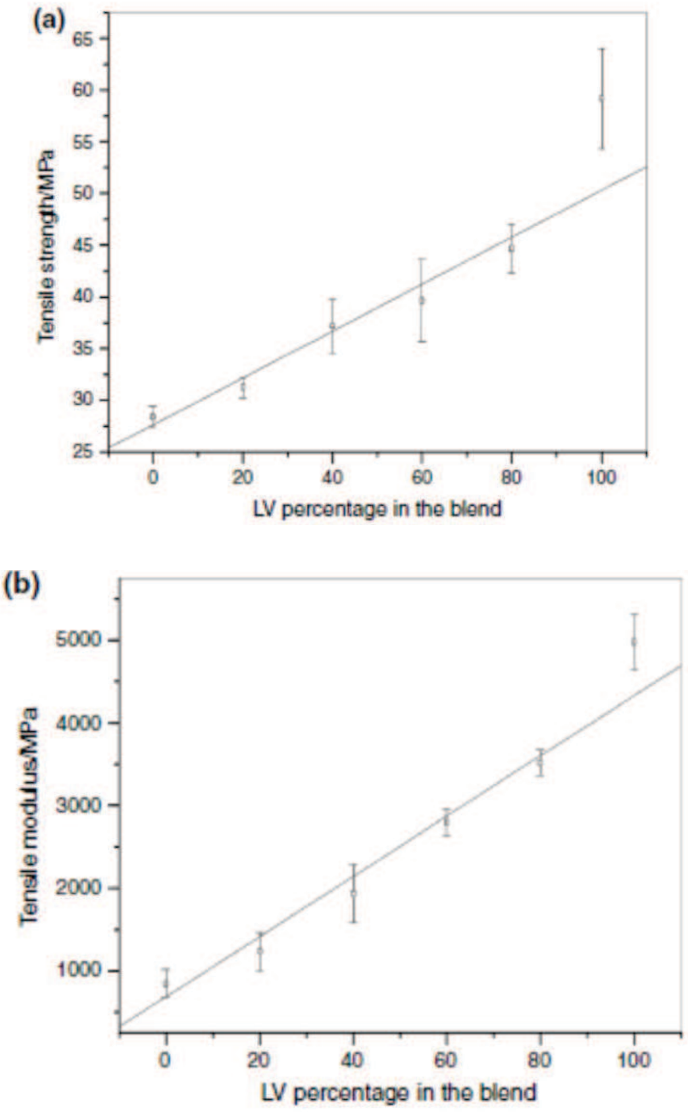


Figure 77- Tensile strength (a) and tensile modulus (b) as function of the LV content in the blend

Figure 78 shows the comparison of the tensile fractured surfaces for pure PP and sample 3. Polypropylene showed a ductile fracture surface with some evidence of filler particles dispersed in. The PP used is a reactor elastomer-modified polypropylene compound. It is well accepted in the literature [38] that polypropylene can be modified with mineral fillers to improve mechnical properties. Sample 3 (Fig. 78b) shows no clear sign of phase separation confirming the good compatibility achieved with the studied formulations. Graupner et al. [39] demonstrated that non-polar groups of lignin can interact with PLA and PP by van der Waals' forces and by the interaction of lignin with cellulose through its ester groups and the anhydride of MAPP via dipoles and hydrogen bonds, respectively. These confirm tensile testing findings, which showed a clear strengthening effect with increased LV content. Therefore, the Liquid Wood used in the present study is thought to act as an efficient reinforcing agent for the studied PP blends thanks to the presence of PLA and MAPP in the final formulation.

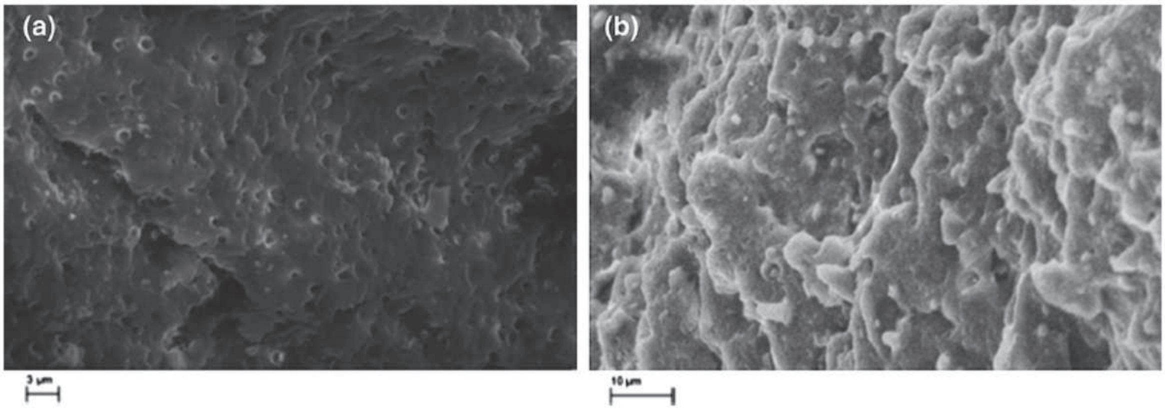


Figure 78- SEM images of a pristine polypropylene and b sample 3

Calorimetric characterization has demonstrated the presence of polylactic acid in Liquid Wood that is probably added by Tecnaro, to improve the mouldability of LV without compromising its green character. According to the aim of this work, the obtained thermogravimetric results suggest that the use of polypropylene as matrix for wood blends should not limit the processing temperature of the Liquid Wood and overall does not anticipate the degradation of lignin in the blends thus leading to obtain a perfect marketable PP/LV system. Moreover, the mechanical properties of the blends showed consistent performances increases with LV additions which can be valuable for their practical use. These increases were explained in the framework of the improved compatibility arisen from the combined presence of PLA, lignin and MAPP in the blends.

5.5.4 Biobased recyclable epoxy composites

In order to overcome the limited recyclability of commercial HP-RTM resins we selected a novel technology patented by the company Connora Technologies (Pastine, 2012). This technology relies on the use of cleavable amines named Recyclamine 301 that bring chemical moiety which allow to be selectively broken in mild conditions leading to the conversion of epoxy networks into reusable thermoplastics (Fig. 79). These amines can be reacted with epoxy monomers to form the first truly recyclable epoxies. The amine and epoxy monomers selected are characterized by a fast reaction rate, which makes them suitable for HP-RTM in principle. In this paragraph we detail the results of the experimentation carried out.

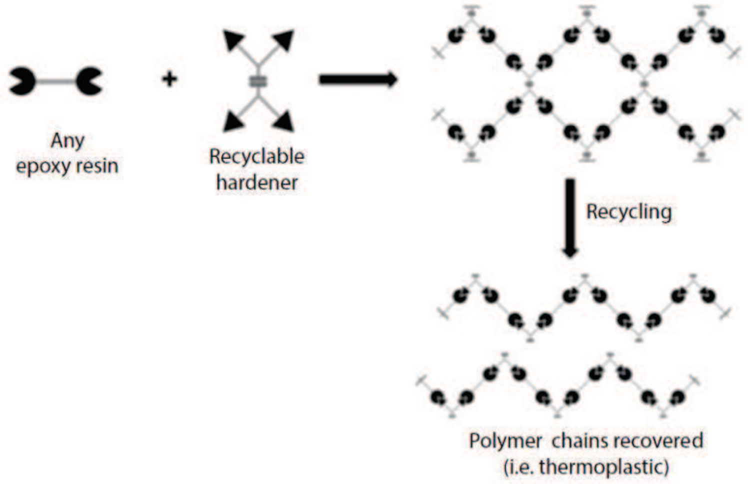


Figure 79 The Recyclamine working principle

The results of DMA testing (Fig. 80) showed that the glass transition temperature shift from 83 °C to 95 °C when precuring time increases from 5 to 15 min. The storage modulus vs temperature curve shows for the sample precured for 15 min higher modulus for all the temperature range analyzed. The DMA test confirms that the resin systems used can be demoulded after only 5 min of precuring. This result makes the system

developed comparable to the commercial resin systems for HP-RTM. However, to gain the Tg values of Huntsman resins recommended for HP-RTM, procuring times of 15 min are best suited. Some precured panels were also postcured in a free standing oven for 1h at 120 °C. Figure 18.10 shows the comparison of the tanδ values for the full carbon specimen before and after postcuring (1). The Tg increased from 88 °C to 102 °C after postcuring. This result showed that for tailoring the cure cycle the systems presented here are comparable to commercial resins.

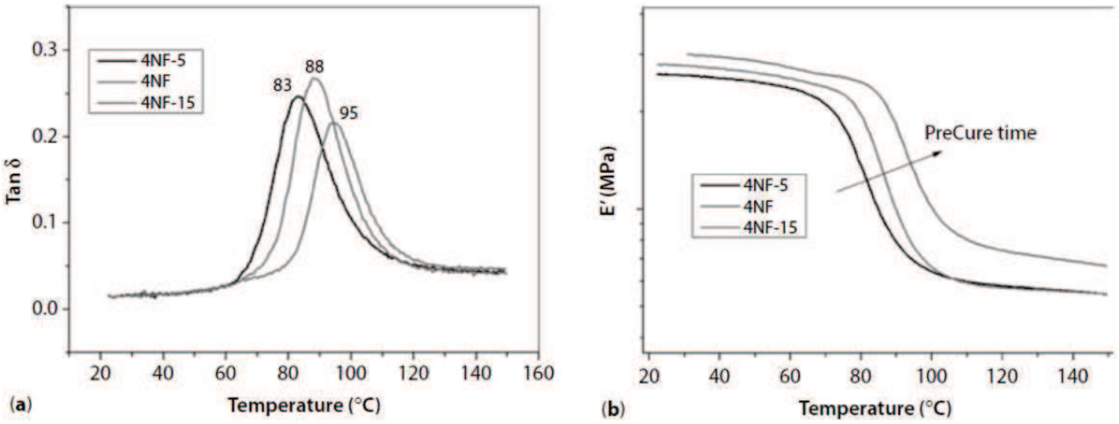


Figure 80- Effect of precuring time: tanδ (sx); storage modulus(dx).

The precured (8 min) samples were thoroughly characterized in terms of their mechanical performances (Fig. 81 and Fig. 82) varying the stacking sequence. The results confirmed, as expected, that carbon fabrics outperformed the natural reinforced fabric with full carbon specimen showing flexural strength 5 times higher than the full natural specimens. The most interesting result is observed when comparing the effect of the stacking sequence because the 3CF/2NF/3CF showed flexural properties comparable to the full carbon specimen. Similar results were obtained in a recent study by Zhang et al. (2013) [40], which explained the good performance of their hybrid glass/flax as the results of the improved stress transfer efficiency on the hybrid interface due to the rough surface of flax fiber and the twisted flax yarn structure. The microscopic analysis of the fractured surface for the tensile specimen 4NF confirms the high level of adhesion of the flax fibers to the resin with extensive formation of resin hackle (Fig. 83).

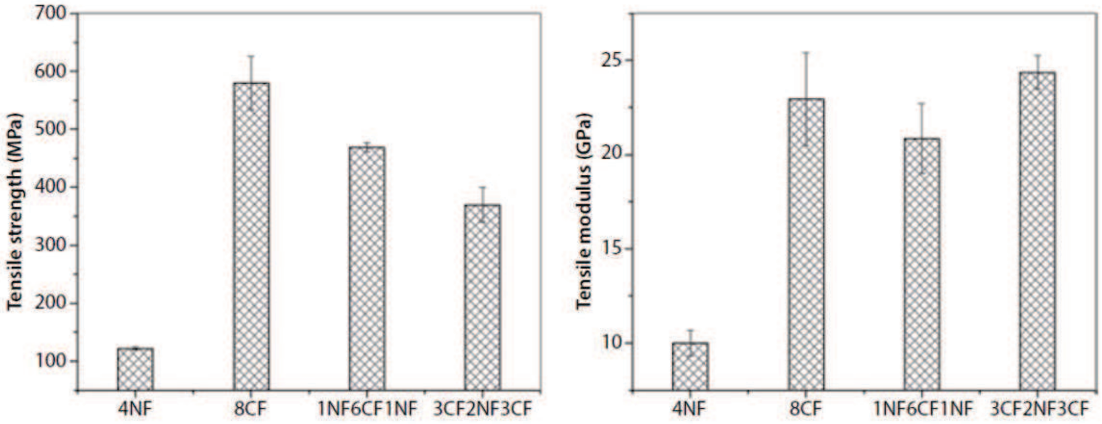


Figure 81- Tensile properties for samples cured for 8min: strength (sx) and modulus (dx).

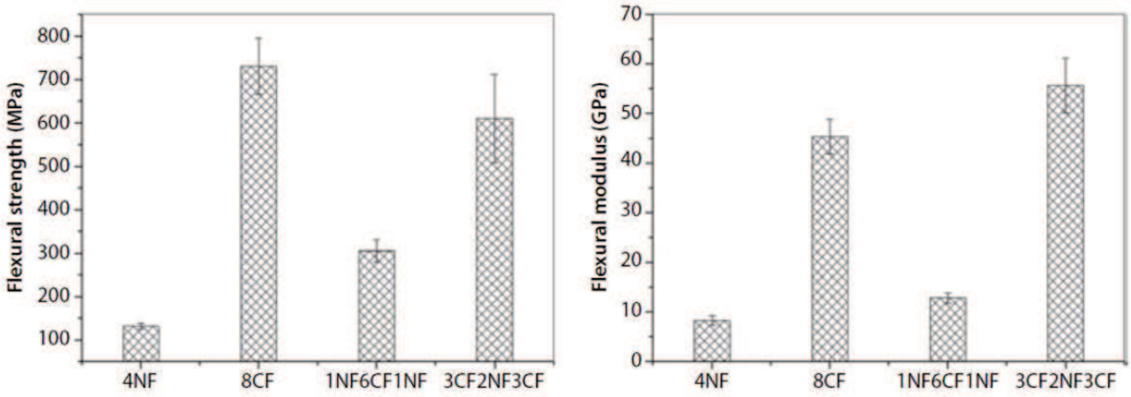


Figure 82- Flexural properties for samples cured for 8 min: strength (sx) and modulus (dx).

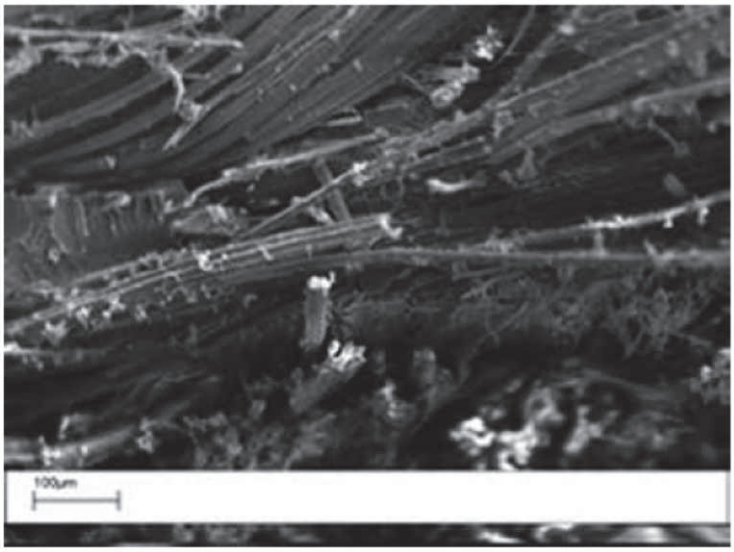


Figure 83- SEM analysis of the fractured tensile specimens 4NF

As outlined in the description of materials and methods the cured epoxy composites can be chemically recycled with a solution of water and acetic acid obtaining two products: the reinforcement fibers and a white solid power. This power is thermoplastic as demonstrated by the rheology test (Fig. 84). The curve display the typical shear thinning behavior of thermoplastic with viscosity decreasing for increasing shear rates. The possible structure of the thermoplastic polymer recovered after the recycling treatment is drawn in Fig. 85. The hypothesis is that a poly-hydroxy amino ether (PHAE) is obtained as the result of selected cleavage of the amine reagent in the acidic medium during the recycling treatment. Poly-hydroxy amino ethers belong to the class of the so called epoxy thermoplastic (White, 2000) [41].

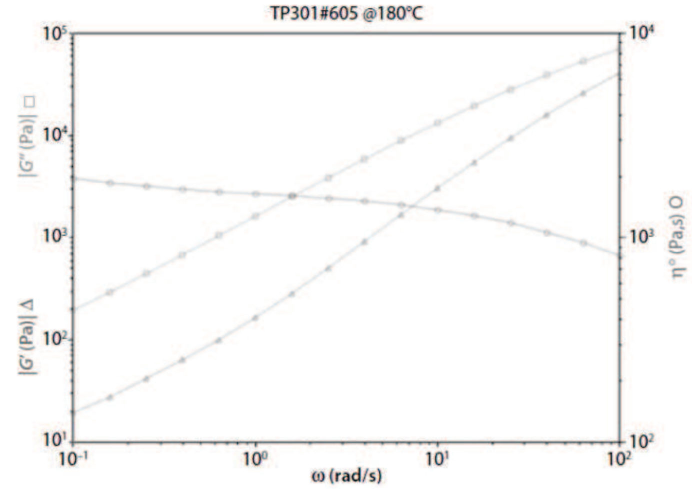


Figure 84- Isothermal frequency sweep for the epoxy thermoplastic recovered from the chemical recycling of the epoxy composites processed by HP-RTM.

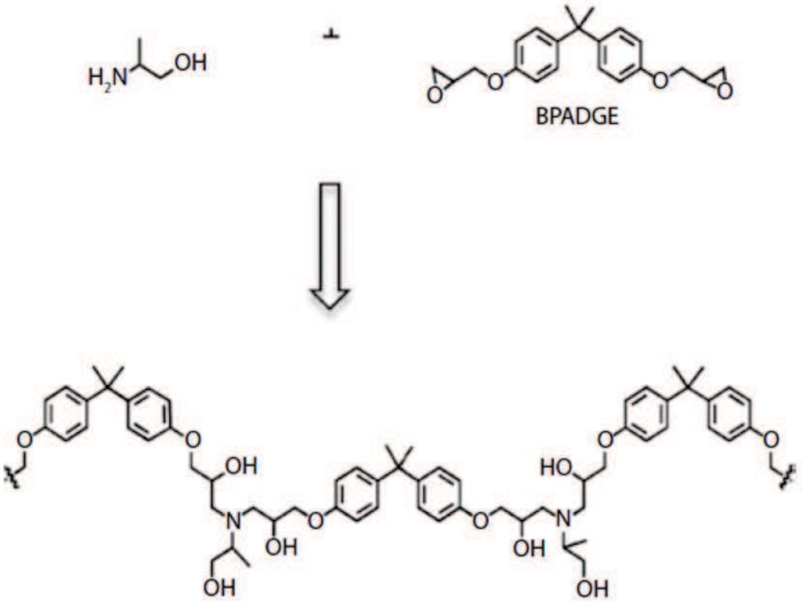


Figure 85- Possible structure of the epoxy thermoplastic starting from the reagents

The recovered thermoplastic was processed by injection moulding into dog-bone specimens that were further characterized by DMA and tensile testing. The

DMA curve is displayed in Fig. 86. The recovered thermoplastic shows a clear glass transition temperature of 74.7 °C as tan δ peak. This value is similar to the Tg values reported by White et al. (2000) for epoxy thermoplastics produced by direct synthesis from monomers. The tensile testing resulted in a modulus of 3.10 GPa and a strength of 10.23 MPa. The modulus found for the recycled polymer is in the same range of epoxy thermoplastic obtained from the synthetic approach but the tensile strength is lower. This result is due to the recycling route which, being based on the depolymerization of a thermoset network, might result in the presence of some low molecular mass oligomers.

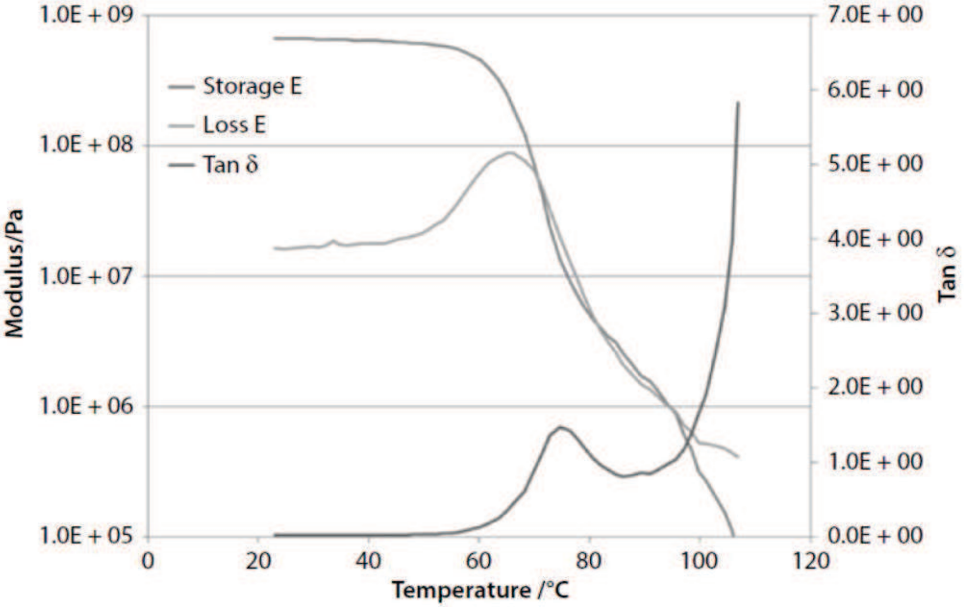


Figure 86- DMA curve for the epoxy thermoplastic recovered from the chemical recycling of the epoxy composites processed by HP-RTM

The present sub-section focused on the development of a novel bio-epoxy formulation for HP-RTM. The resins used in HP-RTM must comply with peculiar requirements in terms of reactivity and viscosity. The review of the state of the art evidenced that commercial resins can be cured and demoulded in very short times, lower than 10 min. These short curing times lead to the use of reactive bicomponent systems that are injected at high pressure. The formulation presented here satisfied the requirements of short demoulding times in the range from 5 min to 15 min. The mechanical properties of the composites analyzed were in the same range of the commercial systems. However, the formulation developed presented two main advantages compared to commercial solutions: the formulation contained a bio-epoxy monomer with up to 48% biobased carbon content; the formulation was fully recyclable into a usable thermoplastic. The high content of biobased carbon for the epoxy and the use of flax as reinforcements make the composites discussed here a unique example of composites material processed by HP-RTM from renewable sources.

Conclusions and future work

The research work performed during the PhD was focused on the development of novel eco-compatible thermoplastic composites. The experimental work was based on the use of two polymer matrices: polypropylene and poly(lactid acid). Polypropilene is not biodegradable but by the addition of a lignin based polymer the carbon biocontent was increased obtaining a formulation readily available and suitable for applications. The results presented on these blends outlined an increased thermal stability and mechanical resistance due to the addition of the lignin based system. This result is promising for the application of this blend in the automotive field. Many automotive parts, such as for example the under hood parts, require improved thermal performances that can be fulfilled by the proposed approach.

To overcome the problem of the use of petroleum based plastic the use of PLA was investigated in the research. PLA can be synthetized starting from sugar resulting in a ecofriendly matrix. PLA can be composted so it is a viable option to improve the ecocompability of polymers. However, PLA has an high cost of production which, since now, limited its acceptance in mass production. Therefore, to reduce PLA cost and, at the same time, improve the mechanical and thermal properties the addition of lignin was studied. The results obtained showed that, as for PP, lignin is a potentially good additive. However, the results showed some processing issues due to the thermal stability of PLA which was negatively affected by the reactive moiety of lignin.

The results obtained confirmed that combining natural fillers (i.e. lignin) with polymers synthetized by natural sources (i.e. PLA) promising blends can be obtained. However, processing should be optimized to minimize the degradation. To achieve such goal, a feasible process could be to chemical modify the lignin structure or the PLA matrix. Lignin is a multifunctional polymers thus, the approach could be oriented to link moiety which can reduce the interaction with the ester group of PLA.

In addition to the improvement of the thermal stability of PLA/Lignin blends future work will be oriented to the use of such blends as matrix for natural fiber composites. This further development will be pursued to obtain sytems suitable for structural applications.

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