3. Structure, properties and recyclability of natural fibre reinforced polymer composites

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Abstract. Natural fibre reinforced polymer composites have emerged as a potential environmentally friendly and cost-effective option to synthetic fibre reinforced composites. In recent years, there has been growing interest in the field of cellulose reinforced thermoplastic and thermoset composites having properties of toughness, resistance to chemical attack and recyclability. Unlike thermoset composites, natural fibres are less frequently used in common thermoplastics such as polyethylene, poly (vinyl chloride) and polystyrene because of difficulties associated with surface interactions between hydrophilic fiber and hydrophobic thermoplastic. Such divergent behavior results in difficulties in compounding these materials and poor mechanical properties. Reports are made on the modification of the polar natural fibre surface by grafting with compatible thermoplastic segments or coating with compatibilizing and coupling agents before the compounding step, addition of compatibilizing and coupling agents in the compounding step, and the modification of the matrix polymer with a polar group. Studies are made on the recyclability and reprocessing of agro based fiber composites and the effect of mechanical and thermal degradation parameters during the recycling processes.

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1. Introduction

Nowadays, the growing environmental awareness throughout the world has triggered a paradigm shift towards designing environmental-friendly materials. Consequently, in recent years, natural fibres have attracted more and more interest as reinforcements for both thermoplastic and thermosetting polymer composites [1-4]. Natural fibres from renewable natural resources offer the potential to act as a biodegradable reinforcing materials alternative for the use of glass or carbon fibres and inorganic fillers. The specific properties of these natural fibres, namely low cost, lightweight, renewable character, carbon dioxide sequesterization, biodegradability, high specific strength and modulus, availability in a variety of forms throughout the world, surface reactivity and the possibility to generate energy, absence of associated health hazards, easy fibre surface modification, and relative non-abrasiveness motivate their association with organic polymers to elaborate composite materials [5, 6]. Biocomposites derived from natural fibres and traditional thermoplastics or thermosets can maintain a balance between economy and environment allowing them to be considered for applications in the fields of automotives, aerospace, defence, marine, sporting goods, building, furniture and packaging industries. These materials provide high durability, design flexibility and lightweight which make them attractive materials in these applications [7, 8]. The versatility, strength and non-corrosive properties of plastics in combination with fibres have helped to establish this class of composites as a potential and viable alternative in several applications. In this chapter we discuss mainly about the structure, properties and recyclability of commonly used natural fibre reinforced polymer composites.

1.1. Natural fibre composites

Natural fibres, used to fill and reinforce both thermoplastics and thermosets, represent one of the fastest-growing types of polymer additives. Fibre reinforced composites (FRC) contain reinforcements having lengths much higher than their cross-sectional dimensions. Fibres are the load-carrying members, while the surrounding matrix keeps them in the desired location and orientation. Natural fibres themselves are cellulose fibre reinforced materials as they consist of microfibrils in an amorphous matrix of lignin and hemicelluloses. These fibres enjoy the right potential for utilisation in composites due to their adequate tensile strength and good specific modulus, thus ensuring a value-added application avenue.

Lignocellulosic natural fibres, originated from different plant fibres are suitable raw materials for the production of a wide range of composites for
different applications. When these fibres are incorporated into a matrix to form a composite, the matrix serves to bind the fibres together, transfer loads to the fibres, and protect them against environmental damage caused by elevated temperature and humidity. The matrix has a strong influence on several mechanical properties of the composite such as transverse modulus and strength, shear properties and properties in compression. The most common matrix materials for composites are thermoset and thermoplastic polymers. The combination of a plastic matrix and reinforcing fibres give rise to composites having the best properties of each component. Since the plastics are soft, flexible, and lightweight as compared to fibres, their combination provides a high strength-to-weight ratio for the resulting composite. The significant weight savings and the ease and low cost of the raw constituent materials make these composites an attractive alternative material to glass and carbon fibres [9]. Material scientists all over the world focus their attention on natural composites reinforced with jute, sisal, banana, coir, pineapple etc., primarily to cut down on the cost of raw materials.

1.1.1. Thermoplastic and thermoset composites

Natural fibre reinforced thermoplastic and thermoset composites constitute an important class of materials with wide variety of applications. Thermoplastic composites are composites that use a thermoplastic polymer as a matrix. A thermoplastic polymer is a long chain polymer that can be either amorphous in structure or semi-crystalline. These polymers are long chain, medium to high molecular weight materials, whose general properties are those of toughness, resistance to chemical attack and recyclability. Simple methods such as extrusion and injection moulding are used for the processing of these composites. An advantage of thermoplastics is that the moulding can be carried out non-isothermally, i.e., they can be rapidly heated and rapidly cooled without any damaging effects to their microstructure. However, polymerized thermoplastics tend to have melt viscosities between 500 and 1000 times that of thermosets, which necessitates higher pressures, causes processing difficulties and adds expenses. In thermoplastics, most of the work reported so far deals with polymers such as polyethylene, polypropylene, polystyrene, and poly (vinyl chloride). The natural fibres used to reinforce thermoplastics mainly include wood, cotton, flax, hemp, jute, sisal, banana, pineapple, rice straw and sugarcane fibres [10].

Thermoset polymers are also used as a matrix material for most structural composite materials. The single biggest advantage of thermoset polymers is that they have a very low viscosity and can thus be introduced into fibres at low pressures. Thermosets are processed by simple processing techniques
such as hand lay-up and spraying, compression, transfer, resin transfer, injection, compression injection, and pressure bag moulding operations. The use of a few other methods, such as cold press moulding, filament winding, pultrusion, reinforced reaction injection moulding, and vacuum forming, is hardly reported in the case of composites [5]. In these polymers, the fibres are used as unidirectional tapes or mats. These are impregnated with the thermosetting resins and then exposed to high temperature for curing to take place. These composite materials are chemically cured to a highly cross-linked, three-dimensional network structure. These cross-linked structures are highly solvent resistant, tough and creep resistant. The major types of thermosetting materials are epoxy resins and unsaturated polyesters (UP); phenolic resins (including phenol-formaldehyde ones); amino resins (e.g. melamine-formaldehyde and urea-formaldehyde ones), and polyurethane.

1.1.2. Structure and properties of composites

A composite may be defined as any substance which is made by physically combining two or more existing materials, selected filler or reinforcing agent and a compatible matrix binder, to produce a multiphase system with different properties from that of the starting materials but in which the constituents retain their identity. The components of a composite do not dissolve or otherwise merge completely with each other, but nevertheless do act in concert. The surface adhesion between the fibre and the polymer plays an important role in the transmission of stress from matrix to the fibre and thus contributes towards the performance of the composite. The properties of the composite cannot be achieved by any of the components acting alone. Overall, the properties of the composite are determined by:

i) the properties of the fibre ii) the properties of the resin
iii) the ratio of fibre to resin in the composite (Fibre Volume Fraction)
iv) the geometry and orientation of the fibres in the composite, and
v) the surface interaction of fibre and resin (the ‘interface’)

i) The properties of the fibre

Properties of natural fibres result from their structure and chemical composition. The essential component of all plant fibres is cellulose. Plant fibres are characterized by their cellular structures. Each cell contains crystalline (i.e. ordered) cellulose regions (microfibrils) which are interconnected via lignin and hemicellulose fragments. A cell has one external wall and three thick side walls. The more parallel the microfibrils are arranged to the fibre axis, the higher is the fibre strength.
Most of the natural fibres have porous structure (seen in cross-section) which can be a factor facilitating their saturation with resins. All of the different fibres used in composites have different properties and so affect the properties of the composite in different ways. The mechanical properties of natural fibres, especially flax, hemp, jute and sisal, are very good and may successfully compete with glass fibre in specific strength and modulus. Natural fibres show higher elongation to break than glass or carbon fibres, which may enhance composite performance. Thermal conductivity of natural fibres is low (0.29–0.32 W/mK), which thereby makes a good thermal barrier.

ii) The properties of the resin

Any resin system for use in a composite material will require the following properties:

- good mechanical properties
- good adhesive properties
- good toughness properties
- good resistance to environmental degradation

iii) The amount of fibre in the composite (‘Fibre Volume Fraction’)

The amount of fibre in the composite is largely governed by the manufacturing process used. However, reinforcing fabrics with closely packed fibres will give higher Fibre Volume Fractions (FVF) in a laminate than will those fabrics which are made with coarser fibres, or which have large gaps between the fibre bundles. Fibre diameter is an important factor here with the more expensive smaller diameter fibres providing higher fibre surface areas, spreading the fibre/matrix interfacial loads. As a general rule, the stiffness and strength of a laminate will increase in proportion to the amount of fibre present. However, above about 60-70 % FVF (depending on the way in which the fibres pack together), although the tensile stiffness may continue to increase, the laminate’s strength will reach a peak and then begin to decrease due to the lack of sufficient resin to hold the fibres together properly.

iv) The geometry and orientation of the fibres in the composite

The geometry of the fibres in a composite is also important since fibres have their highest mechanical properties along their lengths, rather than across their widths. This leads to the highly anisotropic properties of composites, where, unlike metals, the mechanical properties of the composite are likely to be very different when tested in different directions. This means
that it is very important when considering the use of composites to understand at the design stage, both the magnitude and the direction of the applied loads. When correctly accounted for, these anisotropic properties can be very advantageous since it is only necessary to put material where loads will be applied, and thus redundant material is avoided.

v) The surface interaction of fibre and resin (the ‘interface’)

In polymer matrix composites, the interface between the reinforcing phase and the bulk phase is paramount to the overall performance of the composite as a structural material. The quality of the fibre/matrix interface is important in the application of natural fibres as reinforcement in plastics. The interface is called the ‘heart of the composite’ and the composite properties depend on the interface. It is not a distinct phase, as the interface does not have a clear boundary. It is more accurately viewed as a transition region that possesses neither the properties of the fibre nor that of the matrix. The interface has been reported to have distinct properties by researchers [11]. The schematic representation of the composite interface is shown in Figure 1. The ultimate mechanical properties of fibre reinforced polymeric composites depend not only on the properties of the fibres and the matrix, but also on the degree of interfacial adhesion between the fibre and the polymer matrix [12].

Figure 1. Schematic representation of the interface.
The major drawbacks associated with the use of natural fibres as reinforcements in thermoplastic matrix to achieve composite material with improved mechanical properties and dimensional stability are the poor wettability and weak interfacial bonding with the polymer [13, 14]. The polar natural fibre and the non-polar polymer matrix end up in relatively weak bonding. The deficient adhesion leads to a weak load transfer from the matrix to the fibres, which induces a low reinforcing effect. Poor interfacial bonding leads to composites exhibiting rather poor durability and toughness. Another problem is that the processing temperature of composites is restricted to 200 °C as vegetable fibres undergo degradation at higher temperatures; this restricts the choice of matrix materials. Another setback is the high moisture absorption of natural fibres leading to swelling and presence of voids at the interface, which results in poor mechanical properties and reduced dimensional stability of composites. So, in order to reduce the hydrophilic character of the cellulose fibres and to improve their adhesion properties, a pre-treatment of the fibre surface or the incorporation of a surface modifier during processing is required [13, 15]. Several methods used to modify natural fibre surfaces, such as alkali treatment [16, 17], the use of maleic anhydride copolymers [18, 19], pre-impregnation of the fibre [20], and the use of silanes [21-25], have been proposed.

2. Recyclability of natural fibre composites

Current environmental concerns have stimulated interest in the recycling of materials, and plastics in particular. There are two concurrent reasons justifying this: the desire not to waste resources, and the problem of disposing scrap material that may otherwise pollute the environment. Composites, and particularly those based on thermosetting polymers, are often perceived as difficult or impossible to recycle, and for that matter, there have been suggestions that their use should be avoided. Yet, their attractive properties make them likely candidates for an ever increasing use in volume manufacturing, particularly in the automotive industry.

Scientists working in the field of green materials technology, as well as the policy makers are optimistic about the use and usability of natural fibres to develop greener solutions for the production, consumption and disposal of automotive products. Scientists researching in this field have argued that one way to achieve higher recyclability in an environmentally sound manner would be to substitute commonly used synthetic reinforcing materials in polymer composites, such as glass fibres, by natural fibres. The economic aspects and environmental impact of their use cannot be overestimated. As an example of bio-based materials, natural fibres are
lighter than conventional fibre materials and therefore can contribute to cost reduction; their production also being more cost effective. It was found that natural fibre reinforced composites can deliver weight savings of about 50%, and reduce costs by approximately 30%. The widely perceived consumer demands are also part of the commercial logic to invest in green materials research and production. The use of natural fibres is often seen as the panacea for various environmental problems, such as end-of-life (ELV) vehicles, waste minimization, as well as for projects of economic development [26].

Sustainable bio-based eco-products are products with environmental acceptability which are derived from renewable resources with recycling capabilities and triggered biodegradability. Green polymers, also known as bio-polymers, are derived from natural/agricultural renewable resources. Examples for green polymers are thermoplastic starch, polyhydroxy alkanoates (PHA), polylactic acid (PLA), lignin-based epoxy and soy-based resins as well as epoxidised linseed oil. In search for viable ‘greener’ solutions for more environmental-friendly consumer goods, science and industry turn to nature and in particular to natural fibres [26]. Many investigations have been made on the potential use of natural fibres as reinforcements for so-called eco-composites, and in several cases the results have shown that they exhibit good stiffness and promising properties. Renewable resources and recyclable thermoplastic polymers provide an attractive eco-friendly quality as well as environmental sustainability to the resulting natural fibre-reinforced composites [27]. Natural fibres such as kenaf, hemp, flax, jute, and sisal offer such benefits as reductions in weight, cost, and CO₂, lower reliance on foreign oil sources, recyclability, and the added benefit that these fibre sources are “green” or ecofriendly [28].

Growing environmental awareness and new rules and regulations are forcing industries to seek more ecologically friendly materials for their products. In recent years, the development of biocomposites from biodegradable polymers and natural fibres has attracted great interest, because these materials could allow complete degradation in soil or by composting processes and do not emit any toxic or noxious components [27]. Commonly, natural fibre reinforced petrol-based polymers are called green composites. The use of green/synthetic polymers, reinforced by either synthetic or natural fibres respectively, will limit the environmental friendliness of the resulting composite because of the low biodegradability and problems related to the material recycling. By incorporating natural fibres into green polymer matrices, new “truly green” biodegradable eco-composites (also called bio-composites) are created. This class of materials is currently under development and is heavily researched.
The main advantage of “truly green” composites comes with their disposal – these materials are compostable and will provide valuable soil amendment products for a sustainable agriculture. Even when incinerated, truly green composites are said to have no impact on global warming, because the carbon dioxide (CO₂) set free during thermal incineration equals the CO₂ consumed by the crop before harvesting [28].

Glass-reinforced plastics exhibit shortcomings such as their relatively high fibre density (approximately 40 % higher than natural fibres), difficulty to machine, and poor recycling properties; not to mention the potential health hazards posed by glass-fibre particulate [29].

2.1. Recycling of natural fibre reinforced thermoplastic composites

Problems associated with recycling of thermoplastics and their composites are much less compared with the recycling of the thermosets. So the widespread use of thermoplastic composites in various industries over the last decades is expected to have a more favourable environmental impact. Recycled thermoplastic composites, however, show a degradation of their mechanical performance, the extent of which depends both on the recycling process as well as on the service conditions history. Furthermore, the possibility for recycling offers sound economical benefits because of the high price of the virgin material [30].

Amongst eco-compatible polymer composites, special attention has been given to polypropylene (PP) composites, due to their added advantage of recyclability. PP cannot be classified as a biodegradable polymer, but it takes an important place in eco-composite materials. For example, Mohanty et al. have demonstrated that NF-reinforced PP composites have the potential to replace glass/PP composites [31]. Significant research efforts have been also spent on eco-composites based on recyclable polymers reinforced with natural fibres.

It is found that the recycling processes do not induce very significant changes in flexural strength and thermal stability of the composites. In particular, polypropylene-based composites reinforced with kenaf fibres are less sensitive to reprocessing cycles with respect to PP-based composites reinforced with rice hulls. The response of PP-based composites reinforced with rice hulls or kenaf fibres is promising since their properties remain almost unchanged after recycling processes. Moreover, the recycled composites are suitable for applications as construction materials for indoor applications [27]. The effect of the recycling processes on the property retention of the materials is illustrated in Figure 2.
Figure 2. Influence of recycling processes on flexural strength and flexural modulus of (a) PP/RH composites and (b) PP/K composites.

From the above figure, it is very clear that the composites reinforced with kenaf show higher modulus and stress at maximum load with respect to the composites reinforced with rice hulls. The flexural strength of PP/RH recycled composites decreases by about 10% after recycling, although the flexural modulus is practically unchanged. For PP/K composites, the recycling processes induces a slight decrease in the flexural strength after the second recycling (about 5%) and an increase of the flexural modulus (about 20%) [27].

Evstatiev et al. have done studies on exploring the potential of a new type of polymer-polymer composites microfibrillar reinforced composites (MFC) for recycling purposes, in order to obtain material with engineering specifications [32-36].

While natural fibres have been used traditionally to fill and reinforce thermosets, natural fibre reinforced thermoplastics, especially polypropylene composites, have attracted greater attention due to their added advantage of recyclability [37]. A few studies have looked at comparative life cycle assessment of specific components made from glass fibre reinforced (GFR) composite materials and natural fibre reinforced (NFR) composite materials.
The study also reports results from sensitivity analyses with respect to recycling at various percentages, pallet life, plastic content, and changes in transport distances, and finds that NFR pallet is environmentally superior under almost all scenarios. However, the environmental impacts of NFR pallet are worse, if its expected life falls below 3 years, compared to that of 5 years for the GFR pallet.

Recycling involves mechanical and thermal degradation of both the matrix and the reinforcement. Recycling of biocompostable materials limits their environmental impact, while keeping possible waste management by composting. Besides biodegradation, composite recycling could make these materials more interesting and extend their useful life, reducing the global impact on the environment by minimizing raw material consumption and storing carbon for a longer period.

For the matrix PLLA, Pillin et al. studied the thermo-mechanical effects of recycling on the mechanical properties, noting a reduction of stress and strain at break, whereas the Young’s modulus remained constant [42]. Degradation of PLLA can be catalysed at transformation temperature by the presence of air and thus random chain scissions occur [43]. In composites, the mechanical properties of sisal/PP and hemp/PP have been investigated as a function of recycling by Bourmaud et al. [44]. Both tensile modulus and strength were shown to be quite stable after up to seven injection cycles, but the initial value was quite low due to the relatively poor mechanical properties of PP. Many authors have noted a large reduction in fibre length during multiple injection cycles [45-47]. The reduction of dimensions is attributed to shear stresses developed in the injection equipment. Thompson et al. have studied the rheological behaviour of nanofiller/elastomer composites during recycling [48]. Reduction of viscosity during injection cycles was caused by thermo-oxidative degradation, and the destruction of filler networks was highlighted. Reduction of viscosity during injection cycles can be caused by matrix degradation (chain scissions) and/or reduction of reinforcement size.

Duigou et al. studied the recyclability of flax/PLLA biocomposites elaborated with the injection moulding process, and compared their behaviour with that of PP (polypropylene) composites [49]. The evolution of matrix molecular weight and reinforcement geometry during recycling were also been studied. Repeated injection cycles had shown to influence many parameters such as reinforcement geometry, mechanical properties, molecular weight of PLLA, thermal behaviour and rheological behaviour.

Observation of tensile fracture surfaces in the SEM gave qualitative information about fibre dispersion and orientation. After the first injection cycle many bundles of fibres could be noted (Figure 3) and thus a lack of homogeneity compared to the fracture surface of a sample subjected to six
njection cycles (Figure 4). This confirmed bundle division during recycling, and could explain the small change in fibre aspect ratio with injection cycles.

Tensile modulus is only slightly influenced by recycling as illustrated in Figure 5. This trend was also noted during previous tests on hemp and sisal/PP composites [44]. A small reduction of PLLA modulus during recycling, shown by Pillin et al. [42] is one of the reasons for this behaviour. Another is the small decrease of fibre aspect ratio during recycling.

Figures 6 & 7 show that, for both fibre contents, stress and strain at break decrease. This drop may be caused by fibre damage during recycling, the reduction in fibre length resulting in more strain concentrations and a higher risk of debonding.

Figure 3. SEM micrograph of the fracture surface of BC-20 % after one injection.

Figure 4. SEM micrograph of the fracture surface of BC-20 % after six injections.
Figure 5. Evolution of tensile modulus as a function of injection cycles.

Figure 6. Evolution of tensile strength at yield as a function of injection cycles.

Figure 7. Evolution of strain at break as a function of injection cycles.
Although biocomposites become more brittle with recycling (Figure 7), they retain a large part of their properties, at least until the third injection cycle. In an industrial situation, 100% of the recycled biocomposite would not be used (recycled material is always mixed with virgin material).

In order to examine the matrix degradation mechanism, molecular weight of PLLA was investigated as a function of injection cycles. Figure 8 shows the evolution of molecular weight for the biocomposites at different fibre contents compared to neat PLLA. Initially, molecular weight of PLLA was 220,000 g/mol.

During multiple injections, molecular weight of PLLA decreases dramatically. Fibre content plays an important role in reduction of molecular weight of polymer, since the molecular weight decreases rapidly with higher fibre content (-83% for BC-20% and -94% for BC-30%). The chemical structure of PLLA is sensitive to hydrolytic degradation and especially to high temperature [42, 50].

Other kinds of degradation processes will also occur during recycling: depolymerisation of macromolecular chains due to residual catalyst, radical and nonradical reactions, cis-elimination, trans-esterification [50, 51], and mechanical degradation due to interactions of the polymer with the equipment and high shear rate in the injection process. Complex degradation processes result in molecular weight reduction during recycling.

Figures 9 & 10, obtained by DSC, show the influence of injection cycles on glass transition temperature ($T_g$) and melting enthalpy (ΔHm) of the PLLA and the biocomposites BC-20% and BC-30%. All the data are indexed in Table 1.
During the first injection, the presence of fibres causes little change in glass transition temperature (T_g) (Figure 9). These results are confirmed by the work on injected, recycled newspaper fibre/ PLLA bio composites of Huda et al. [52]. A drop in PLLA molecular weight was observed as fibre content and number of injection cycles increased. Higher fibre content appeared to accelerate PLLA degradation during recycling. This drop in molecular weight contributed to the lowering of ultimate biocomposite properties. Calorimetric study showed that, depending on the fibre content, glass transition temperature decreased and degree of crystallinity increased with injection cycles. This evolution could be explained by the degradation occurred during processing which induced higher molecular mobility. Newtonian viscosity of these biocomposites also decreased as a function of injection cycles.
Table 1. Evolution of thermal properties of PLLA, BC-20% and BC-30% as a function of injection cycles.

<table>
<thead>
<tr>
<th>Material</th>
<th>Injection cycles</th>
<th>$T_g$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J g$^{-1}$)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J g$^{-1}$)</th>
<th>$\chi$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA</td>
<td>1</td>
<td>66.5</td>
<td>-</td>
<td>-</td>
<td>123.3</td>
<td>36.5</td>
<td>38.7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>59.9</td>
<td>93.6</td>
<td>15.9</td>
<td>104.3</td>
<td>16.4</td>
<td>41.0</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>56.5</td>
<td>97.7</td>
<td>38.9</td>
<td>89.8</td>
<td>0.6</td>
<td>53.2</td>
</tr>
<tr>
<td>BC-20%</td>
<td>1</td>
<td>61.1</td>
<td>-</td>
<td>-</td>
<td>110.9</td>
<td>36.5</td>
<td>39.7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>56.9</td>
<td>89.1</td>
<td>16.8</td>
<td>90.4</td>
<td>21.6</td>
<td>47.1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>54.9</td>
<td>92.4</td>
<td>41.3</td>
<td>-</td>
<td>-</td>
<td>50.2</td>
</tr>
<tr>
<td>BC-30%</td>
<td>1</td>
<td>62.2</td>
<td>114.5</td>
<td>45.6</td>
<td>-</td>
<td>-</td>
<td>47.0</td>
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<tr>
<td></td>
<td>3</td>
<td>57.8</td>
<td>112.5</td>
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<td>6</td>
<td>41.7</td>
<td>87.1</td>
<td>35.9</td>
<td>85.1</td>
<td>5.1</td>
<td>43.2</td>
</tr>
</tbody>
</table>

$T_g$, $T_c$, $\Delta H_c$, $T_m$, $\Delta H_m$ and $\chi$ represent, respectively, the glass transition temperature, the crystallization temperature, the crystallization enthalpy, the melting temperature, the melting enthalpy and the degree of crystallinity.

Figure 11. Evolution of Newtonian viscosity as a function of injection cycles.

Figure 11 presents the evolution of Newtonian viscosity as a function of the number of recycling processes for PLLA, BC-20% and BC-30%. During the first injection, it may be noted that for higher fibre content, the viscosity is higher. Several authors have noted that as fibre content increases chain mobility of PLLA is restricted, which may be due to the fibre–polymer and
fibre–fibre interactions [53-56]. During recycling, the viscosities of BC-20% and BC-30% decrease (Figure 11). This viscosity drop, either for PLLA, BC-20 % or BC-30 % is very significant, indicating a high degradation rate of the PLLA matrix. Molecular weight reduction (also shown by SEC), reduction of fibre length and aspect ratio are the phenomena that explain this observation. Several authors have described the influence of the length and L/d ratio of fibres on the viscosity of composites [53, 57].

This emphasizes the degradation of the matrix (reduction of molecular weight) through chain scission mechanisms during recycling. With natural fibres as reinforcements, end-of-life composting is possible. Complementary work on degradation mechanisms and their link to environment (temperature, humidity, etc.), as well as detailed damage threshold identifications are in progress.

### 2.2. Recycling of natural fibre reinforced thermoset composites

The polymer–polymer interface is a vital factor which plays a crucial role in the ability of polymer composites, especially thermoset polymers and polymer composites, to be repaired, recycled, and bonded [58].

Thermoset matrix recycling is of course unfeasible because of the thoroughly cross-linked nature and the inability to be remoulded. Nevertheless, technologies are now being developed that can reprocess scrap composites to recover some of the value in the material and thus avoid the need of disposing the solid in a landfill, which has been the only option until recently.

### 2.3. Recycled fibre as reinforcements

Kouparttsas et al. [59] have investigated the feasibility of reusing short fibres recovered from recycled thermoset composites for the production of new composites. Glass fibres were recovered from glass-polyester composites, and carbon and aramide fibres from epoxy based composites. In most cases examined, recycling does not adversely affect the mechanical performance of the new composite. This overall behaviour is explained in terms of length preservation, fibre dispersion mechanism and fibre-matrix adhesion. There are positive conclusions drawn from their investigation on the feasibility of reusing short recycled fibres recovered from thermoset composites [59].

### References