EFFECT OF RECYCLING ON NATURAL FIBRE POLYPROPYLENE COMPOSITES REGARDING THE CRYSTALLIZATION BEHAVIOUR AND FIBRE LENGTH DISTRIBUTION

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Abstract
Fibre’s shape and active surface area supposed to have an impact upon resulting mechanical properties of the natural fibre reinforced thermoplastic composite. These values are also influenced by multiprocessing steps such as the cascade of extrusion and injection moulding due to fibre breakage.
Nevertheless, regarding the energetic benefit of natural fibres, these composites are used e.g. to substitute other materials in applications bearing minor engineering purpose. Concerning end of life, these composite can be processed *via* feedstock recycling instead of energy recovery. The influence of these additional processing steps in terms of thermal properties and viscosity behavior of the natural fibre composite are depicted. Here, the detection is done by DMA measurements, flow length determination *via* a spiral mould and high pressure capillary rheometer. The observed behavior is correlated to the fibre’s shape in the polymer matrix detected by QICPIC, an image analysis sensor.

1. Introduction

Due to their different properties compared to other materials, natural fibres thermoplastic composites (NFTC) have gained increasing interest in different industrial applications. Nevertheless, their application is presently limited to structures having a low mechanical level. Besides inner linings at doors or trunks in automobiles, they are processes to yield helmets, boats, etc.
Generally, the major proportion of natural fibres as reinforcement material is processed in compression moulding technique, whereas extrusion and injection moulding play a minor role in forming the desired structure.
Especially, regarding the feedstock recycling containing the processing steps of grinding, sorting and reprocessing to form structures, compression moulding reprocessing results in structures having much lower mechanical properties than before the recycling step. Here, natural fibre reinforced composites are e.g. used as patch limitation in gardens. This “downcycling” is typically connected to the knowledge that natural fibres themselves have low mechanical properties, a low fibre-matrix-adhesion, minor thermal stability, etc.
Nevertheless, regarding the end of life, recycling gets more and more an obligatory issue to go along with the environment protection measures like the European regulation No. 525/2013. However, there

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is still a great deficiency about the multiprocessing effects on new categories of materials, such as natural fibre reinforced thermoplastic composites.
Besides the fact of less thermal stability compared to other reinforcement materials, natural fibres are supposed to be processed with low melting thermoplastic materials, such as e.g. polypropylene. Here, primers have to be added to overcome the difference in polarity between fibre and matrix and create the required adhesion to yield higher mechanical properties. In case of polypropylene, maleic anhydride-*grafted*-polypropylene (MAPP) is used as an industrial standard component.
Processing of naturals fibres in extrusion or injection moulding reveals a part of their special behavior. Besides the fact that shearing energies have the ability to shorten reinforcement fibres, they split the natural fibres prior to shortening [1]. This decrease in fibre diameter has the potential to increase the aspect ratio of the fibre and consequently improve the mechanical properties. Nevertheless, prior investigations have shown, that due to the new created active area at the fibre's surface having free hydroxylic groups the expected increase is not detected for bast fibre flax [2].
All these changes in fibre's shape and distribution [3] as well as adhesion between fibre and surrounding matrix have an influence on the melting and flowing behavior of the composite's melt on the one hand and crystallization and mechanical properties to form the desired structure on the other.

2. Experimental

An industrial extruded polypropylene composite, reinforced by 30 wt.-% sisal fibre, containing stabilizer and primer was injection moulded to form required test specimen. After storage of an appropriate number of specimen, the remaining material was shredded and re-injection moulded again. This multistep processing (feedstock recycling) was performed four times in total.
Regarding each injection step, two different kinds of test specimen were produced: bar-like specimen used for DMA measurements were manufactured using Arburg Allrounder 220 S-150/60, ARBURG GmbH + Co KG, Loßburg, Germany, whereas an Arburg Allrounder 320 C-600/250 was used for the spiral production to result in the determination of the flow length.
Concerning the rheological, thermal and mechanical properties, tests are carried on the raw and the recycled samples (i.e. viscosity *via* high pressure capillary rheometer by GÖTTFERT, flowability using a spiral mould, glass transition temperature and mechanical behavior by DMA Q800 as well as melting and crystallization results by DSC measurements using a DSC Q2000, both systems by TA Instruments).
The change in fibre shape with respect to fibre length and diameter is monitored by cutting small parts at certain positions along the spiral injected products. The samples were than extracted at elevated temperature with decaline and the fibre dimensions of the residue measured by dynamic image analysis sensor, QICPIC, SYMPATEC GmbH, Clausthal-Zellerfeld, Germany. Additionally, microscopy pictures of specimen surfaces were taken by an digital microscope VHX-500, KEYENCE Corporation.

3. Results

The results of the DMA measurements of the different materials in the range between glass transition range and melting temperature at a frequency of 1 Hz are depicted in Figure 1.
It is notable that, after several reprocessing steps, the storage modulus is increasing, following the same trend indicating that the multiprocessing is not downcycling the material but improving the mechanical properties.

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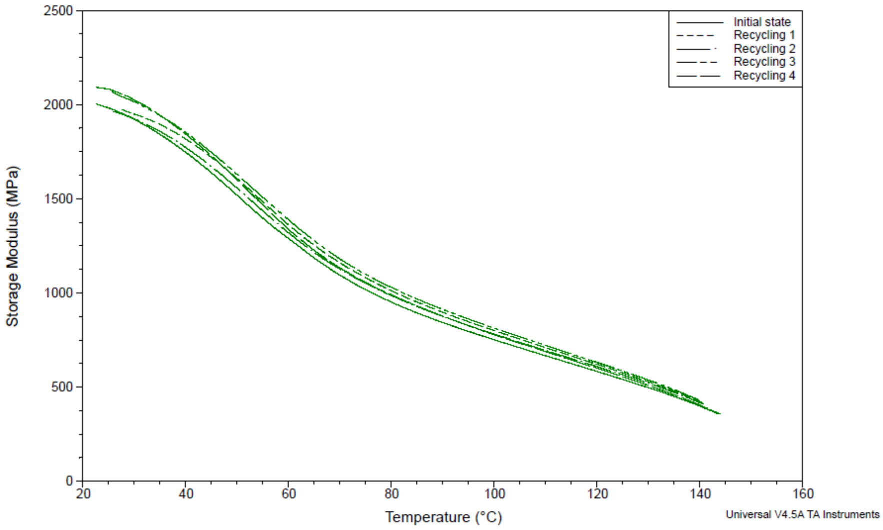

Figure 1. Temperature dependency of storage modulus

Table 1 lists the results of the DSC investigations of the five materials obtained by heat-cool-heat treatment.

Table 1. Melting and crystallization temperatures and enthalpies

Material	Melting Temperature (°C)	Crystallization Temperature (°C)	Melting Temperature (°C)	Melting Enthalphy (J/g)	Crystallizat. Enthalphy (J/g)	Melting Enthalphy (J/g)
Initial state	165,1	124,4	164,3	60,4	64,7	63,6
Recyc. 1	167,4	124,5	164,9	60,6	65,8	64,2
Recyc. 2	164,9	125,1	164,3	60,8	64,1	62,3
Recyc. 3	164,6	125,4	164,3	62,1	63,8	62,3
Recyc. 4	165,5	125,5	164,3	62,8	64,8	63,7

This table points out that the composition of the material changes by injection moulding between initial state and first recycling step (Recyc. 1). The second and third injection moulding of reprocessed material show similar results for temperature and enthalphies as well, whereas the last recycled material differs slightly from the ones before.
The flowability of the systems, determined by the flow length in a spiral mould, shows comparable results (Fig. 2). Here, the flow length increases significantly from initial state to Recyc. 1-material, indicating a better flowability of the reprocessed material, probably caused by a better distribution. Further processing steps do not increase the value whereas it can be stated that the flowability remains to a certain extent constant.

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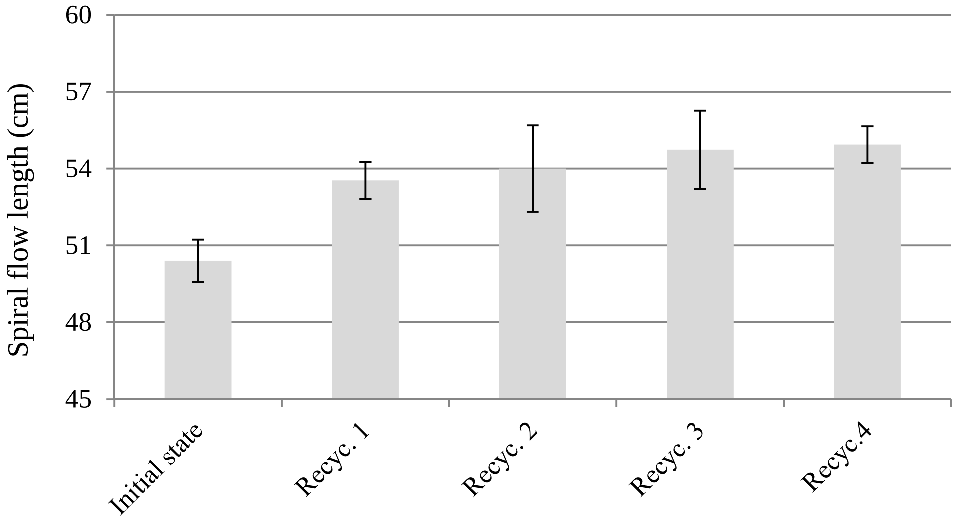

Figure 2. Spiral flow length in injection moulding process

To prove the above mentioned results, measurements using a high pressure capillary rheometer were performed. Also here, the results show no significant differences, especially at higher shear rates (Fig 3). At a shear rate of 40.000 1/s, all viscosities have a value of approx. 4 Pas, leading to a comparable behavior.

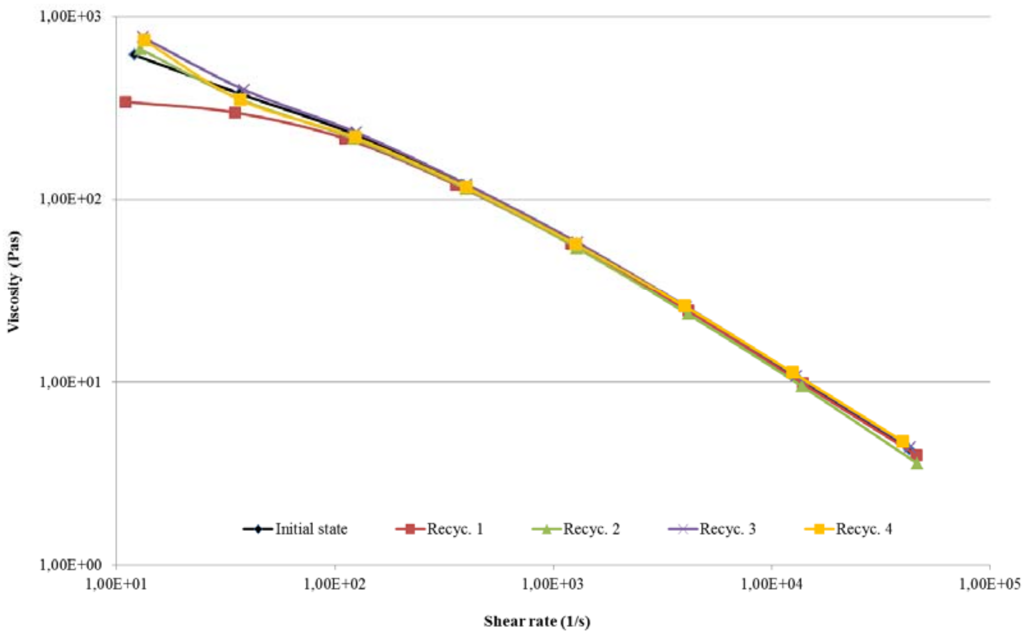

Figure 3. Viscosity curves of investigated materials

Regarding the present results, no significant difference can be detected if the sisal fibre reinforced thermoplastic composite is reprocessed several times.

To evaluate the influence of the multiprocessing steps, the fibre length and diameter are determined *via* dynamic image analysis sensor QICPIC. Therefore, the injection moulded test specimen were divided in four sectors (Fig. 4, red arrows show the injection path) and the matrix was dissolved to yield the imbedded fibres.
The obtained results of the fibre length and diameter are depicted in Figures 5 and 6.

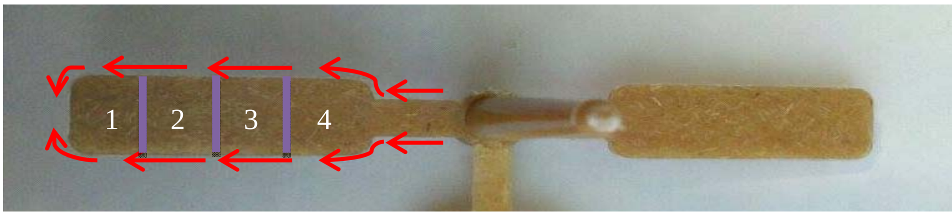

Figure 4. Test specimen

By regarding the average fibre length it can be stated, that the fibre in sector 1 are longer than in sector 4. Also it can be seen in the figure that fibres are shortened by reprocessing.

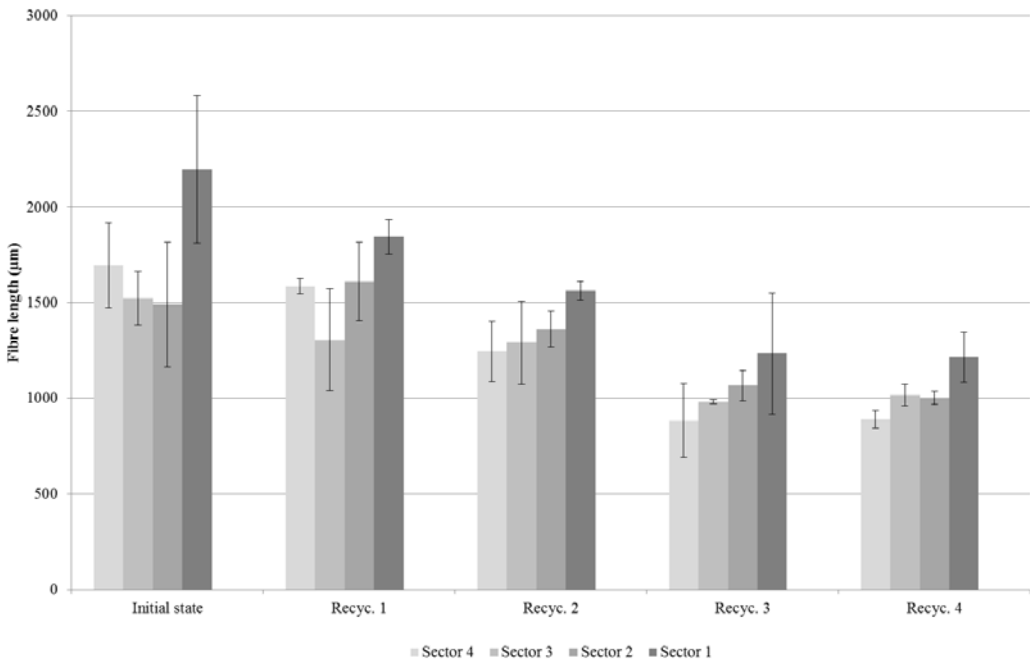

Figure 5. Sisal fibre length

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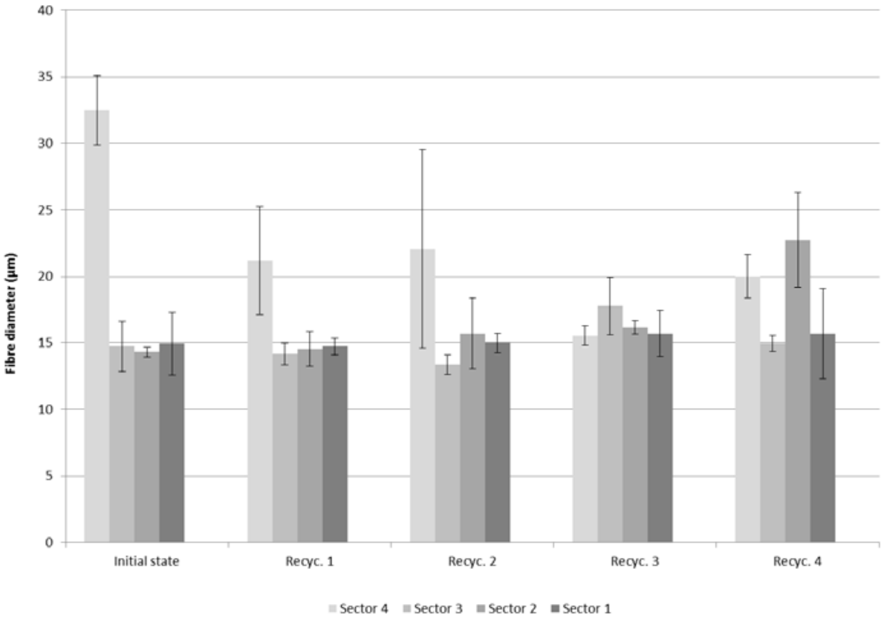

Figure 6. Sisal fibre diameter

In case of the diameter, sector 4 shows higher values compared to the other sectors. Also it can be stated that for the first reprocessing cycles, sectors 1 to 3 show approx. the same values. Further reprocessing steps reveal some inhomogeneities.

In total, the aspect ratio (relation between fibre length to fibre diameter) of the sisal fibres changes from above 100 for the initial state to under 50 for reprocessing step 4 (“Recyc. 4”), indicating that the mechanical properties should be lowered, too.

Nevertheless it was shown in Figure 1, that the mechanical properties increase if the material is reprocessed which can be indicated by smaller fibres or better distribution inside the composite.

Additionally, this could have to more reasons: one is the additional crosslinking of the fibres by the primer system leading to fibre agglomerations, the second is the improved crystallization behavior of the matrix through the fibres indicated by transcrystallization on the fibre’s surface.

To have a look upon the fibre’s shape in the compund, microscopy was performed. The results of a comparison of the sample’s surface picture of the sector 2 at initial state and reprocessing step 4 is shown in Figure 7.

Here, the whole cut area of the specimen is divided in four regions, totally leading to the specimen’s surface. It can be noticed that the fibre’s distribution in the initial state is less than in the reprocessed state and that the fibres in the later state seem to be shorter. Also, in reprocessing 4, the fibres are more oriented in flow direction that in the initial state which is also positively influencing the mechanical properties in DMA measurements.

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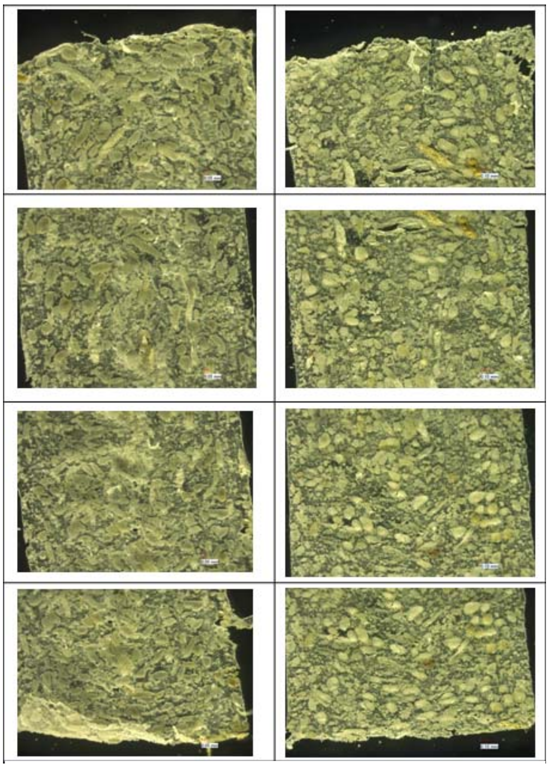

Initial state Recyc. 4

Figure 7. Microscopic images of section surface

4. Conclusions

The multistep processing of sisal fibre reinforced polypropylene composite reveals interesting material behavior of the fibre under shear. Besides the typical fibre breakage over the range of reprocessing, these fibers also can be splitted to generate a new active surface area along the fibre length, but to a much minor extent compared to bast fibres.

It also has to be stated that in case of sisal fibre reinforcement, the performance results in an increase of the mechanical properties in DMA measurement, which is due to the better distribution of the fibres in the surrounding thermoplastic matrix and the orientation in flow direction.

In contrast, no influence on the thermal behavior of the composite regarding melting or recrystallization processes could be detected. Additionally to that, the rheological properties remain the same, whereas a better flowability in the injection mold could be obtained after the first processing cycle which is supposed to be related also to the better distribution caused by shorter/thinner fibres.

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