



ELSEVIER

Thermochimica Acta 337 (1999) 169–177

thermochimica
acta

www.elsevier.com/locate/tca

Thermogravimetric and differential scanning calorimetric analysis of natural fibres and polypropylene

B. Wielage^{a,*}, Th. Lampke^a, G. Marx^b, K. Nestler^b, D. Starke^b

^aDepartment of Composite Materials, Chemnitz University of Technology, 09107 Chemnitz, Germany

^bDepartment of Chemistry, Chemnitz University of Technology, 09107 Chemnitz, Germany

Received 3 May 1999; received in revised form 10 June 1999; accepted 11 June 1999

Abstract

The thermal behaviour of variably separated flax and hemp fibres was characterised by means of thermogravimetric and differential scanning calorimetric analyses. Reference measurements of cellulose served to describe the degradation behaviour. Furthermore, thermoanalytic investigations on polypropylene were carried out to evaluate the thermal stability and the respective activation energy of the materials. The results prove the thermal stability necessary for the consolidation process of composite materials. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: TGA; DSC; Natural fibres; Polypropylene; Kinetics

1. Introduction

Demands for the saving of fossil resources and for relieving the strain on disposal sites and the atmosphere must be taken into account when developing and using new materials. For lots of applications in the field of lower mechanical loads renewable raw materials are increasingly used as strengthening components for innovative products as an alternative to the use of established fibres (glass-fibre, carbon-fibre) [1]. Flax (on account of its strength) and hemp (because of its high amount of straw and fibres) are presently predominantly applied in Germany. Suitable matrix materials for natural fibre reinforced polymers are resin systems, thermoplastic starch and polyolefins (PE and PP), while polypropylene provides most of

the advantages with regard to economic (price), ecological (recycling behaviour) and technical requirements (higher thermal stability than polyethylene). Injection moulding and consolidating of hybrid non-wovens are suitable procedures to process natural fibre reinforced polymers into sophisticated 3-dimensional parts.

Natural and synthetic polymers are subject to a degradation of the mechanical properties under the influence of increased temperatures [2].

It is very important to have knowledge about the influence of the processing temperatures in relation to the processing duration because there is always thermal stress during the manufacturing of natural fibre reinforced composite materials with thermoplastic matrices. Essential statements regarding the thermal stability of the natural fibres to be processed are obtained from the thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses.

*Corresponding author. Fax: +49-371-531-6179

E-mail address: bernhard.wielage@wsk.tu-chemnitz.de (B. Wielage)

Apart from the determination of thermodynamic data of the reactions it is possible, with the help of thermal analysis, to make statements regarding kinetics. For example, the activation energy E , calculated for the initial stage of pyrolysis, was measured in a range of 150 kcal/mol (628 kJ/mol) for some samples of cellulose. The high activation energies obtained for cellulose were considered to correspond to the highly ordered structure of cellulose [3]. A possible correlation is expected as flax and hemp consist of about 70% of cellulose. However, the authors do not yet dispose of a sufficient number of measurements for hemp so that for the time being it is not possible to reliably determine the activation energy. Preliminary curvatures lead to the assumption that there is a complex reaction mechanism taking place.

2. Experimental

2.1. Materials

1. Rough hemp, separated by ultrasound,
2. Retted flax,
3. Retted flax, separated by steam explosion (DDA),
4. Cellulose (micro-crystalline),
5. Polypropylene PP FH1000,
6. Polypropylene PP FV10DO (grafted with 1% maleic anhydrid).

Rough hemp is an unretted natural fibre material that has not undergone an enzymatic fibre separation. Through the use of ultrasound it was possible to separate the fibres to a degree sufficient for technical, non-textile applications. The examined flax had been won by means of field retting. Retted flax fibres show a lower percentage of fibre companions.

The high-quality DDA flax results from an additional steam explosion treatment using a slightly alkaline soaking solution. DDA flax contains the lowest amount of fibre companions and hurds and consequently shows the largest specific surface. Microcrystalline cellulose was used as a reference material. The polypropylenes are woven, partly crystalline fibres made of isotactic PP. Sample 6 has additionally been grafted with maleic acid anhydrid in order to increase the adhesion to the hydrophile natural fibres.

2.2. Techniques

Cellulose, retted flax, DDA flax and polypropylene were investigated with the help of thermal analysis methods. The degradation of the materials mentioned have been observed by means of a thermogravimetric analysis using a Perkin Elmer model TGA 7 with helium (flow rate 30 ml/min) and with air (flow rate 20 ml/min). A differential scanning calorimetry (Perkin Elmer Pyris 1) was applied for determining the enthalpies. A flow rate of 20 ml/min N_2 was realised. The sample was encapsulated in an aluminium pan (volume 30 μ l) with one hole in the top.

The experimental conditions for the determination of the activation energy (kinetics) were: 30 ml He/min; mass of samples (1–5 mg). The heating rate varied between 2 and 15 K/min.

3. Results and discussion

3.1. Thermogravimetry

Retted flax specimens were thermogravimetrically analysed in a temperature interval of 160°C to 260°C under air atmosphere. It was heated up by 40 K/min in order to attain the isothermal temperature. Fig. 1 shows the results obtained over a period of 2 h. First of all, the hydrophile fibres are subject to a dehydration process in which course 5–8% of adsorbed water will be removed by the processing gas. The amount of adsorbed water is dependent on the ambient humidity. In accordance with the literature [4,5] it has been established that there is no degradation taking place until 160°C. Above this temperature thermal stability is gradually decreasing and decomposition of the fibres occurs.

The polypropylene fibres PP FH1000 (no low-molecular coupling agent) which in this case are used as matrix for flax fibre reinforced composite materials were investigated with the same isothermal test programme. Above the melting temperature of about 160°C (Fig. 2) the polymer is subject to a thermal degradation that is both dependent on time as well as on temperature. Adding antioxidant agents allows to shift the start of the degradation process towards higher temperatures.

In Fig. 3 the change of weight due to temperature for the reference material cellulose is compared with

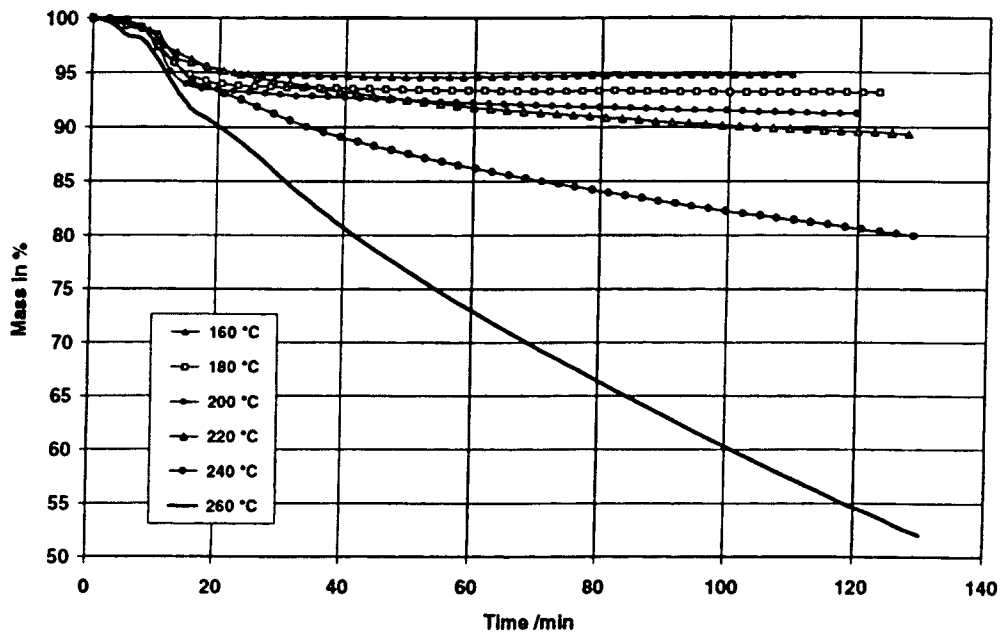


Fig. 1. Isothermal TGA of retted flax, air.

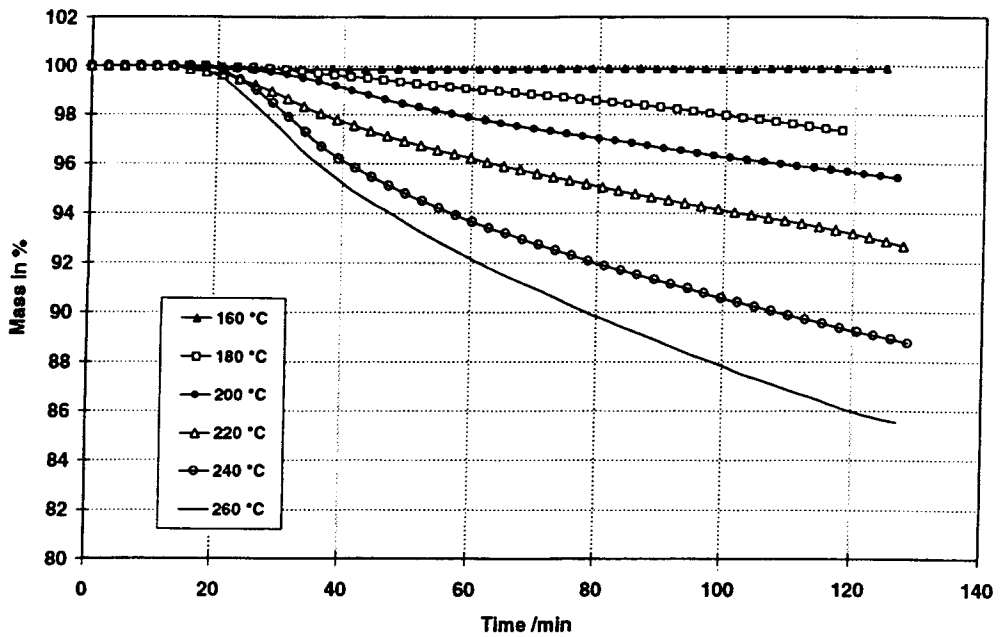


Fig. 2. Isothermal TGA of PP Asota FH1000, air.

retted flax and PP Asota FH1000. Flax is more hydrophile than cellulose. Because of the existing fibre companions the change of weight of flax is more

differentiated than that of cellulose. In this case, the calculated higher onset-value for flax is not a suitable indicator for the gradually starting decomposition

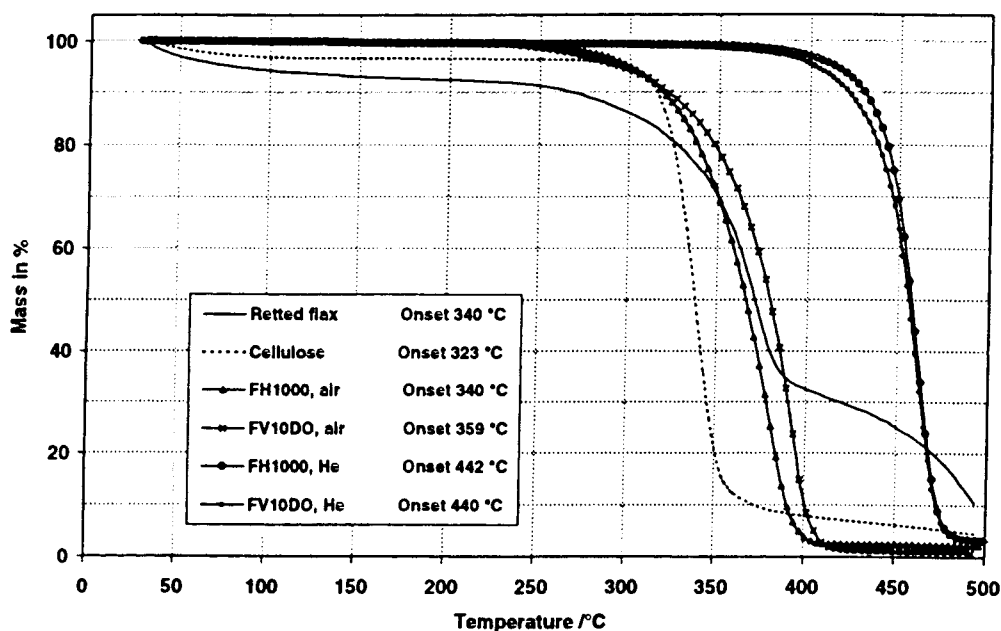


Fig. 3. TGA of retted flax and cellulose, air, PP Asota FH1000 and FV10DO, air and helium, heating rate 10 K/min.

reaction compared with the later starting but more rapidly taking place decomposition reaction of cellulose. According to [6,7] hemicelluloses are generally thought to decompose first, followed by cellulose and lignin. Major [8] claimed that degradation in a dry oxygen atmosphere at 170°C is a result primarily of oxidation, with oxygen acting as a non-specific oxidant. These reactions take place primarily in the amorphous regions of the cellulose, and continue to occur after the degree of polymerization becomes constant. Consequently, the thermal behaviour of flax is consistent with the low crystallinity of its fibre [9,10]. In the presence of air, however, increasing orientation decreases the pyrolysis rate, apparently by limiting the permeability of the cellulose to oxygen [11]. In addition, the containing amount of impurities may initiate more active sites and accelerate the beginning of thermal degradation.

Fig. 3 also proves the thermal stability of both untreated polypropylene fibres and those modified with maleic acid anhydride in dependency on the surrounding atmosphere. The low percentage of grafted MAH (1%) does not have a decisive influence on the thermal behaviour of the polymer. In air atmosphere, thermal decomposition starts at about 100°C

earlier than in inert atmosphere. It is therefore advisable to carry out the process under protective gas conditions when processing thick-walled component parts.

Fig. 4 shows the TGA and DTG graphs of differently separated natural fibres. After the retting the fibres have to be separated either mechanically or wet-chemically. Since every mechanical treatment is damaging the fibres, and fibre companions like hemicelluloses, pectin, lignin, and waxes are only removed insufficiently, separation by steam explosion has gained a special significance. Within certain limits it is possible to achieve fibres with defined properties [12]. Resulting from the low percentage of the above mentioned companions DDA flax shows an increased thermal stability.

3.2. Kinetic evaluation

The kinetics of exothermic reactions are important in assessing the potential of both materials and systems for thermal exposition. The calculation of the kinetic parameters took place in accordance with ASTM E 698-79 [13]. It is possible to check quickly and reliably whether the rate-determining step of the

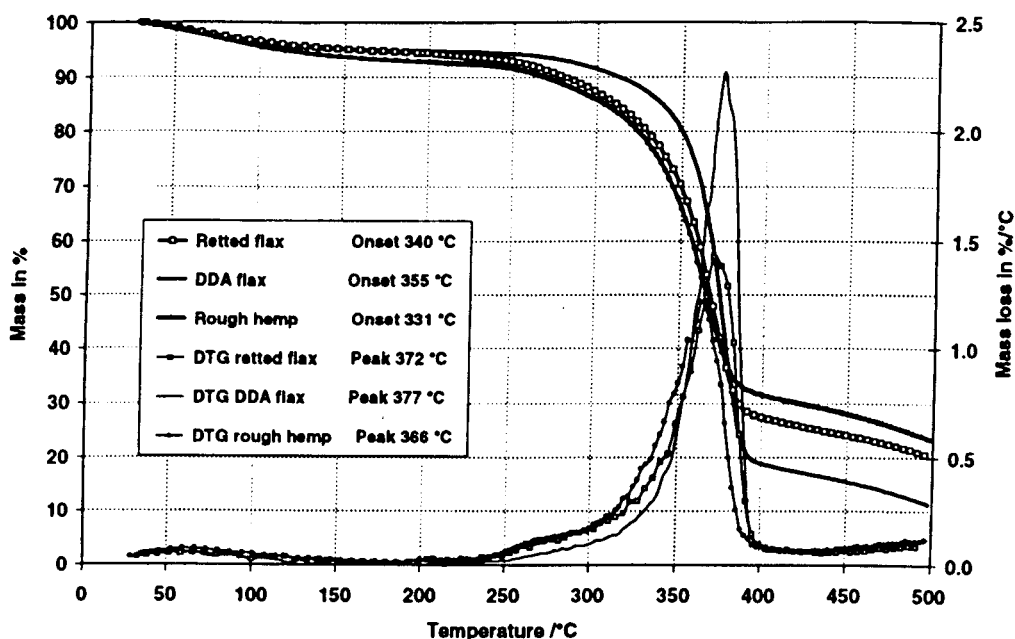


Fig. 4. TGA of retted and DDA flax, rough hemp (separated by ultrasound), 30–200°C: 40 K/min, 200–500°C: 10 K/min, helium.

degradation reaction describes a first-order reaction and does therefore go along with the Arrhenius formulation:

$$E \cong -2.19R[d \lg_{10}\beta/d(1/T)]$$

where E is the activation energy in J/mol, β the heating rate in K/min, T the corrected peak maximum temperature in K and R the gas constant, 8.32 J/mol.

Heating rates of 2, 4, 5, 7, 10, 12 and 15 K/min were chosen, since it is known [14], that higher heating rates pretend activation energies that are too low because of heat transfer problems.

Fig. 5 shows the degradation of DDA flax at the chosen heating rates. It also clearly proves the shifting of the DTG maxima up to the higher temperatures

when increasing the heating rate. If the logarithm of the heating rate is plotted above $1/T$, it is possible to calculate the activation energy from the slope of the regression line. The temperatures used were about the DTG peak maxima. This corresponds to a weight loss between 15% and 75%.

Fig. 6 shows the Arrhenius formulation of DDA flax, cellulose and the two sorts of PP at a weight loss of 45%. Table 1 reveals the activation energies for the above mentioned materials.

The decomposition temperature was found to increase from 270°C to 340°C, in a sequence of DDA flax < cellulose < PP Asota. The calculated kinetic parameters correlate with the results from the TGA (Fig. 3).

Table 1
Results of thermal degradation using ASTM-E 698

	E_{approx} (kJ/mol)	$E/RT_{\text{(approx)}}$	E_{corr} (kJ/mol)	Standard deviation
Cellulose	203.048	39.200	203.106	6.31
DDA flax	188.770	34.637	187.486	3.79
PP Asota FH1000	271.462	44.246	273.045	4.55
PP Asota FV10DO	239.420	39.237	239.488	8.12

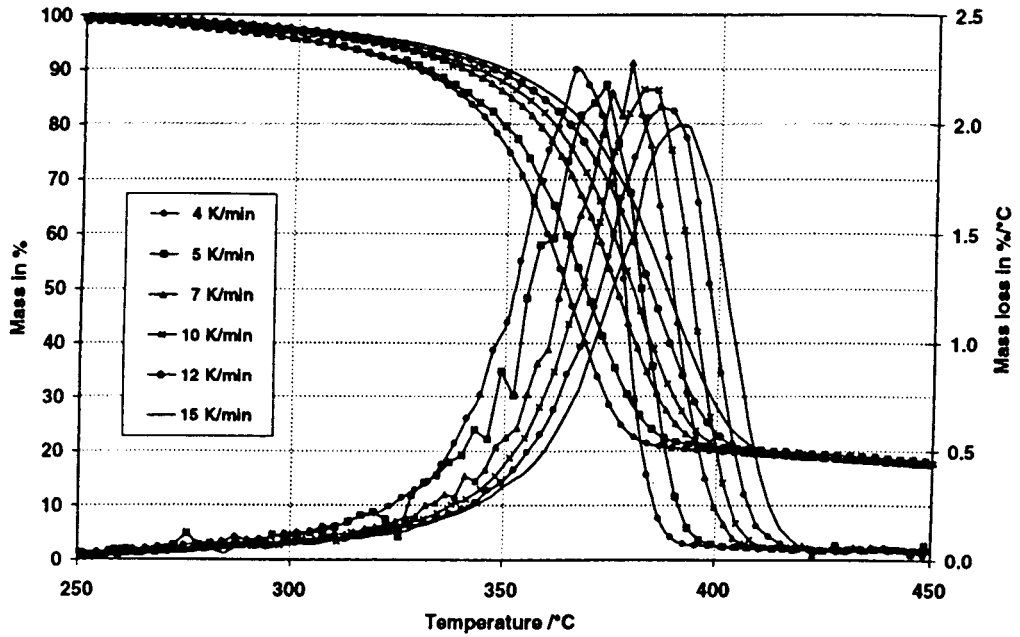


Fig. 5. TGA and DTG of DDA flax, heating rates 4–15 K/min, helium.

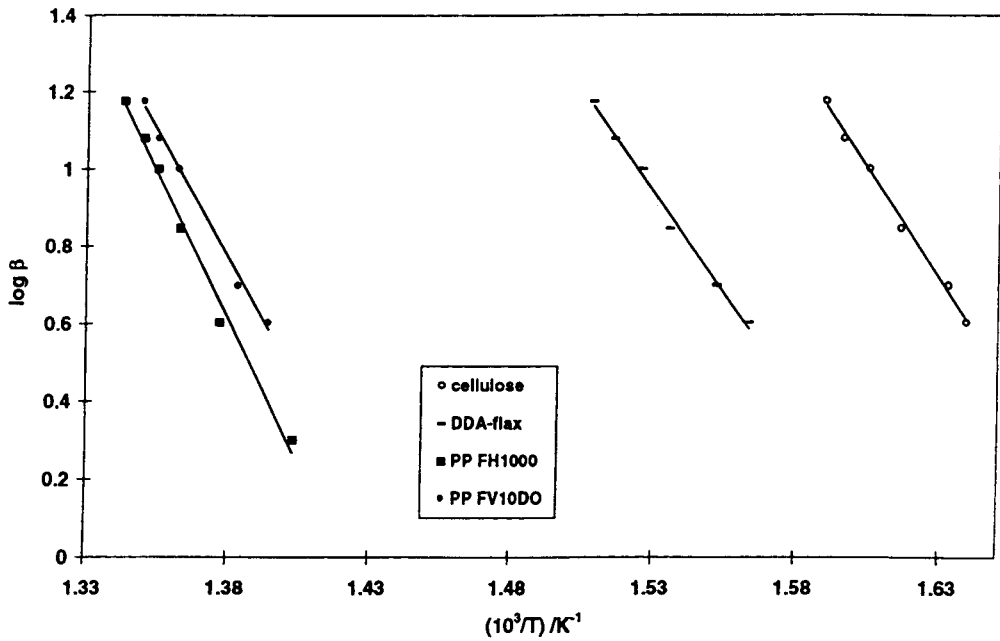


Fig. 6. Arrhenius formulation in accordance with ASTM E 698 at 45% mass loss.

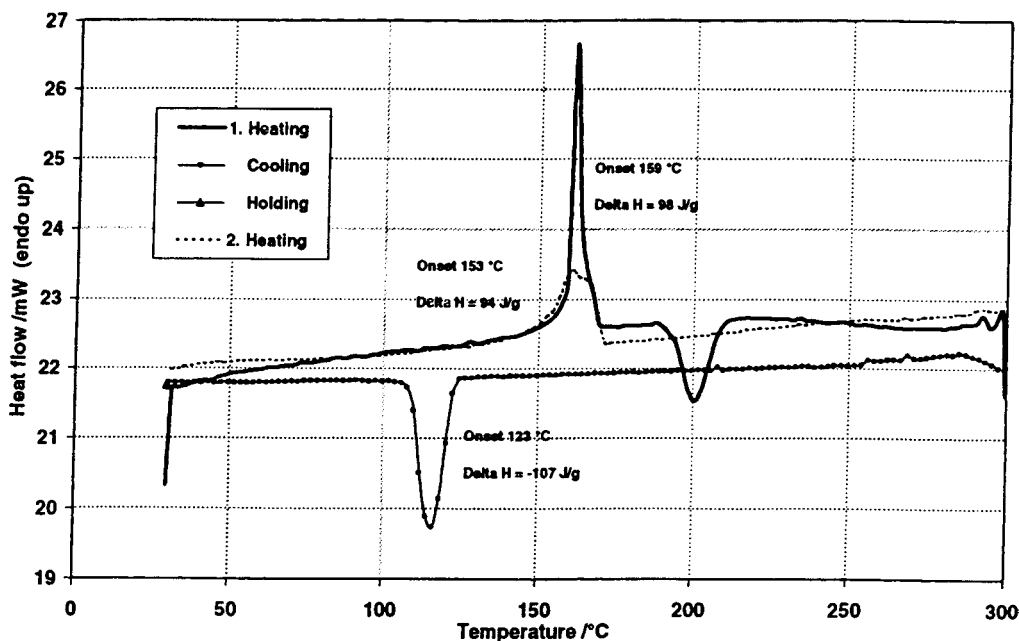


Fig. 7. DCS of PP Asota FH1000, heating rate 5 K/min, nitrogen.

3.3. Differential scanning calorimetry

The polypropylene used was characterised with a heating rate of 2, 5 and 10 K/min by means of DSC. Fig. 7 gives an example of the results at 5 K/min. The melting range of the polymer is visible as an endothermic peak. The material demonstrates an onset value at 159 °C and a specific melting heat of 98 J/g. The exothermic peak in the temperature range of about 200 °C cannot be explained conclusively. The repeated measurement after cooling down and holding the temperature at approximately 30 °C does not show an exothermic reaction. The melting peak does also vary its position and form. Both the lower onset temperature (153 °C) as well as the ΔH of 94 J/g can be traced back to the improved heat transmission in the pan and to the neutralisation of the history of the polymer. The measured melting range of the matrix material is the least possible temperature to process natural fibre reinforced polypropylene successfully.

The examinations of the decomposition of retted flax and cellulose were carried out by means of DSC at a heating rate of 10 K/min in a nitrogen atmosphere (Fig. 8). Thereby cellulose reveals a distinct endother-

mic peak in the temperature interval between 303–345 °C. It is more difficult to determine the endothermic peak of flax because it takes a very flat course. The reaction correlates with both the rapidly falling (cellulose) as well as the continuously slightly decreasing (flax) graph of the change of weight and temperature as determined by the TGA.

In accordance with [15], the above mentioned endothermic reaction of cellulose takes place by two competing pathways. The first is a depolymerization process which leads to an intermediate product, levoglucosan, which further decomposes to various volatiles, e.g. aldehydes, ketones, furans, pyrans. The second pathway is a dehydration process which mainly produces char residue, water and carbon oxides.

3.4. Mechanical properties evaluation

Natural fibres like flax and hemp show a wide distribution of their mechanical properties, e.g. tensile strength, strain and E-module. Separation procedures and additional treatments as well as test conditions (clamping length, test speed) have a decisive influence on the above mentioned properties [16,17].

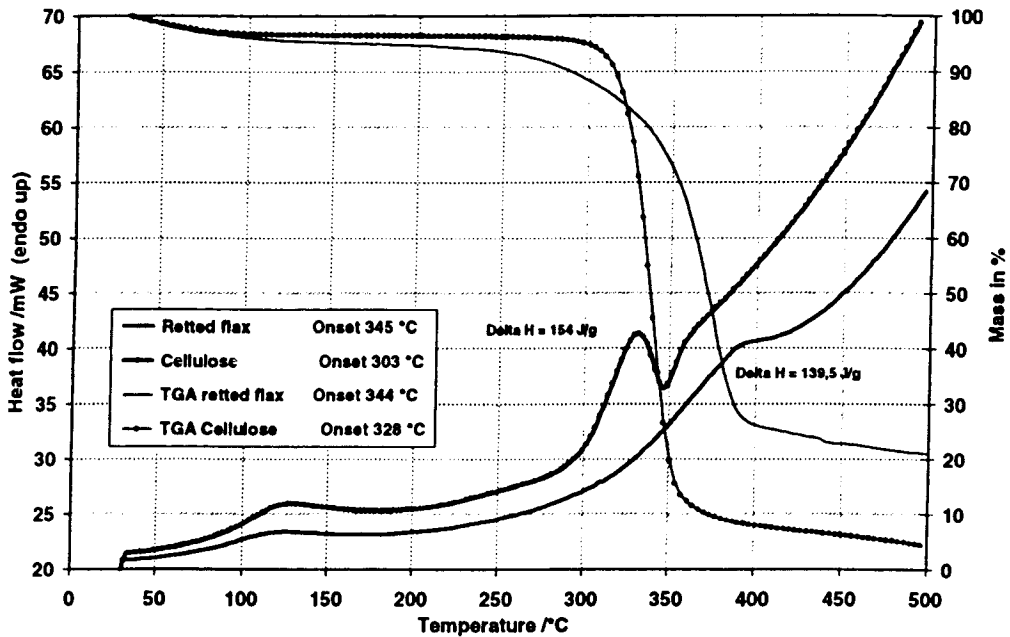


Fig. 8. DCS of retted flax and cellulose, heating rate 10 K/min, nitrogen.

A degradation of the mechanical properties of the fibres occurs under increased temperatures. Exposed to air atmosphere, single fibres of flax have been thermally treated at 180°C, 200°C and 220°C for a time period of 15, 30, 45 and 60 min. The determination of tensile strength takes place in a single fibre tension module at a clamping length of 10 mm. The decrease of tensile strength owing to the higher temperature and duration of exposure can be seen clearly in Fig. 9.

There is a correlation with the results of the isothermal TGA. The influence of temperatures higher than 180°C outweighs the influence of the exposure duration.

When comparing the results of isothermal TGA on flax and polypropylene with the phenomenon stated above, a reduction of the processing duration will in any case have a favourable influence on fibre and matrix properties.

4. Conclusion

Thermogravimetric and differential scanning calorimetric analyses of flax, hemp and polypropylene

prove the thermal stability of these materials. Making use of air, the mass of natural fibres decrease slightly between 200°C and 220°C, above this temperature irreversible degradation of the fibres occurs. The decrease of the mechanical properties of thermally treated flax fibres was investigated by single fibre tensile tests. The results determined for the activation energy of cellulose correlate with the results of extensive, recent investigations [14]. The exemplarily described results on DDA flax prove that, according to the TGA graph, a lower activation energy for the thermal decomposition is necessary.

By means of well chosen processing parameters, in particular temperature and pressure, and the use of suitable coupling agents compounds with good mechanical properties are created.

Taking these influences into account, natural fibre reinforced composites can be manufactured successfully using injection moulding or consolidating of hybrid non-wovens. They represent a suitable material which is an alternative to glass fibre reinforcements for lots of applications in the field of lower mechanical loads.

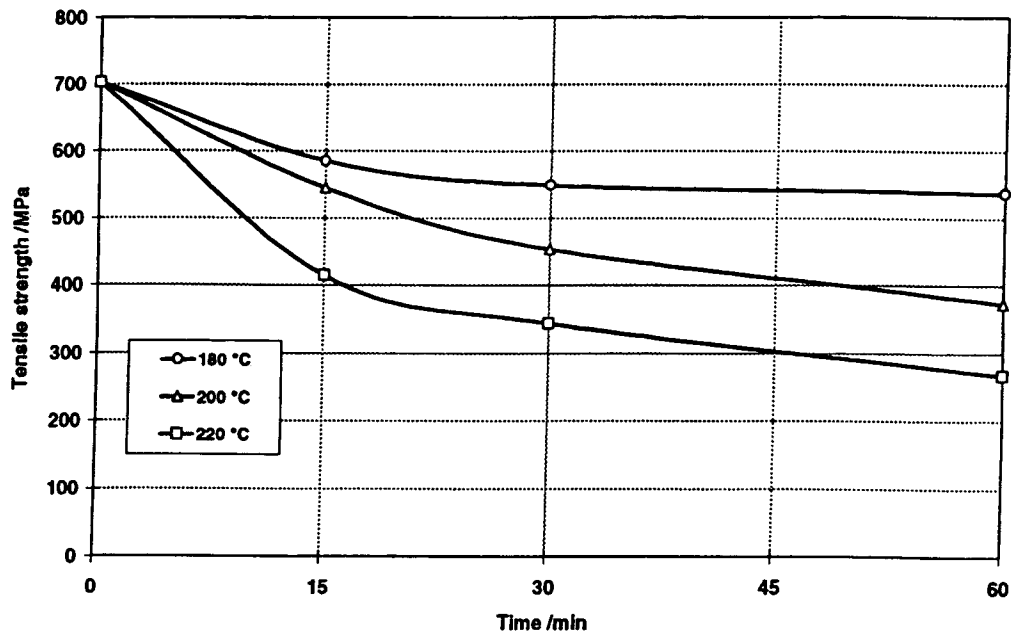


Fig. 9. Thermal degradation of retted flax fibres.

Acknowledgements

The authors thank the Deutsche Forschungsgemeinschaft (DFG, Bonn) for the financial support of the investigations presented.

References

- [1] Th. Kretschmer, J. Kohlhoff, *Werkstoffe in der Fertigung* 5(97) (1997) 3.
- [2] M. Munker, *Werkstoffe in der Fertigung* 3 (1998) 15.
- [3] M.V. Ramiah, *J. Appl. Polym. Sci.* 14 (1970) 1323.
- [4] A.K. Bledzki, J. Gassan, *Natural Fiber Reinforce Plastics, Handbook of Engineering Polymeric Materials*, New York, 1997, 810.
- [5] J. George, S.S. Bhagawan, S. Thomas, *J. Thermal Anal.* 47 (1996) 1121.
- [6] R.A. Susott, *Forest Sci.* 28(4) (1982) 839.
- [7] P. Szabó, G. Várhegyi, F. Till, O. Faix, *J. Anal. Appl. Pyrol.* 36 (1996) 179.
- [8] W.D. Major, *TAPPI* 41(9) (1958) 530.
- [9] P. Yang, S. Kokot, *J. Appl. Polym. Sci.* 60 (1996) 1137.
- [10] A. Basch, M. Lewin, *J. Polym. Sci.* 11 (1973) 3095.
- [11] A. Basch, M. Lewin, *J. Polym. Sci.* 12 (1974) 2053.
- [12] R. Kohler, R. Kessler, 5. Internationale Tagung, Stoffliche Nutzung nachwachsender Rohstoffe Chemnitz, 28/29 October 1998, 51.
- [13] ASTM E 589-79 (1979) 603.
- [14] G. Várhegyi, M.J. Antal, E. Jakab, P. Szabó, *J. Anal. Appl. Pyrol.* 42 (1997) 73.
- [15] A.A. Pappa, N.E. Tzamtzis, M.K. Statheropoulos, G.K. Parissakis, *Thermochim. Acta* 261 (1995) 165.
- [16] R. Kohler, M. Wedler, *Technische Textilien, Mittex* 3 (1996) 7.
- [17] H. Rennebaum, C. Hoyer, E. Grimm, *Erzeugung, Aufbereitung und Verarbeitung von Naturfasern für nichttextile Zwecke, VDI/MEG Kolloquium Agrartechnik* 22 (1997) 68.