J Mater Sci (2009) 44:4379–4382
DOI 10.1007/s10853-009-3656-8

Determination of the fibre volume content in natural fibre-reinforced composites by ultimate analysis

T. Mahrholz · U. Riedel

Received: 11 March 2009 / Accepted: 1 June 2009 / Published online: 14 June 2009

Abstract Natural fibre-reinforced plastics (NFRP) with renewable polymers as matrices are expected to be an increasing market in the future. In this context the quantification of natural fibre volume content in composites is an important parameter for manufacturers to check the laminate quality. This paper reports a new time and cost efficient method for the determination of natural fibre volume content with a good reproducibility. The measurement of the natural fibre volume content is attributed to the quantification of the total carbon content of the composite as sum parameter determined by chemical ultimate analysis never used for fibre-reinforced plastics before. The differentiation of resin matrix and natural fibre is possible by accounting the different carbon fractions of both components. The fibre weight content can be determined from the detected total carbon of the test samples after the measurement of a calibration line from mix standards. Based on the known densities of the natural fibre and of the resin matrix, the fibre weight content is converted into the corresponding volume content. The fibre volume content of porous and also compact composite parts can be calculated by this approach. The fibre volume content can be measured by this method with a standard deviation of ±1%.

Introduction

Currently the market for thermosetting fibre composites is dominated by glass fibre-reinforced plastics (GFRP) [1]. In addition to their potential for light-weight construction and good mechanical characteristics, the low cost of raw materials for glass fibres has contributed to their widespread use. More recently, the critical discussion about the preservation of natural resources and recycling has led to a renewed interest in natural materials with the focus on renewable raw materials [2]. In the automotive industry components previously made with glass fibre composites are now being manufactured using environmentally friendly composites [3]. Fibre composites based on renewable raw materials can offer some specific benefits with regard to environmental impact. For example, thermosetting natural fibre-reinforced plastics (NFRP) exhibit material properties comparable to glass fibre-reinforced composites, but are significantly lighter [4]. They consist of plant fibres such as hemp, jute or flax that are embedded in a polymer matrix. After usage these composites can be readily disposed through raw materials recycling or energy recovery (carbon neutral). Many papers have been published regarding the mechanical properties of natural fibre-reinforced composites (NFRP) based on various thermosets and thermoplastics as matrices [4–7].

In particular, the mechanical properties of natural fibre-reinforced composites (NFRP) depend on their fibre volume content. Thermal and chemical analysis methods for determining the fibre volume content like those that are well-established for glass fibre composites [8] cannot be used for NFRP. A number of methods are described in the literature for quantifying the natural fibre content in thermoplastics and thermosets. Appropriate methods based on soxhlet extraction, X-ray scattering (WAXS), micrographs and solid state NMR spectroscopy as well as near-infrared spectroscopy (NIRS) are included [9, 10]. Mostly these techniques are very time consuming and cost intensive. Moreover, they show in some cases only a low reproducibility. This paper

T. Mahrholz (✉) · U. Riedel
German Aerospace Centre (DLR), Institute of Composite Structures and Adaptive Systems, Lilienthalplatz 7, 38108 Braunschweig, Germany
e-mail: thorsten.mahrholz@dlr.de

presents for the first time the chemical ultimate analysis as a simple and cost efficient analysis method for the determination of the fibre content never used for fibre-reinforced plastics before. Here the volume content of natural fibres of NFRP is derived from the determination of the total carbon content as a sum parameter. A precondition for this is that the natural fibre and the biopolymer must not have identical carbon contents. This requirement is generally fulfilled due to their different chemical structures.

Material and methods

The suitability of chemical ultimate analysis as a quick and highly reproducible analysis method for quantification of the fibre volume content of NFRP laminates is examined. This is done by producing NFRP test plates of hemp/flax non-woven material (25/75) and a biopolymer (linseed-oil acrylate) using a moulding technique. The fibre volume content varies between 25 and 50 vol.%. Quantification of the fibre volume content by means of ultimate analysis was based on the determination of the total carbon content as a sum parameter. After creation of a calibration line based on mix standards (fibre and matrix), the fibre weight content can be calculated based on the detected total carbon content of a test sample. The known densities of the natural fibre and of the biopolymer matrix are used to convert the fibre weight content into the corresponding volume content. In this way the fibre volume content of both porous and compact NFRP can be calculated.

Production of the test plates and test specimens

Fibre mats with dimensions 200 × 200 mm^2 are cut from the hemp/flax semi-finished product (25/75; made by the German company Agrodienst). The cutouts are vacuum dried (1×10^{-2} mbar) over night at 70 °C. A linseed-oil acrylate (Mercryl LT; Hobum Oleochemicals; Germany) is used as the biopolymer which is radically co-polymerized with methacrylic acid (Fluka; Germany) (80 wt% Mercryl LT; 20 wt% methacrylic acid; 2 wt% BK initiator; 2 wt% PAT651 (internal mould release agent)). The number of fibre mats calculated for a fibre volume content of 25 and 50 vol.% is stacked between two cover plates together with the necessary spacer plate. Each layer of fibre semi-finished product is impregnated with the biopolymer resin without bubbles. The entire layer structure is then packed in foil (Hostaphan) and cured in a press at 120 bar and a temperature of 130 °C for 15 min. Next, the NFRP laminates are demoulded and trimmed. At least three square sample pieces with an edge length of approx. 4 × 4 cm are sawed from the test plates. Smaller sample piece geometries are also conceivable. Sampling is performed evenly over the width of the component along the component diagonals.

Preparation of the calibration standards

The cured pure biopolymer resin and the natural fibre semi-finished product are shredded separately in a mill with cutting blades. After that the granulates are pulverized in a ball mill. The pulverized samples are vacuum dried (1×10^{-2} mbar) at 70 °C over night. The moisture-free powders of the matrix and the natural fibres are used to prepare pure and mixed standards with 0, 20, 40, 70 and 100 wt% fibre weight content. The samples are homogenized on a vibrator table in a dry atmosphere, after which the calibration line is calculated by means of the total carbon content determined by ultimate analysis. The sampled test pieces are likewise vacuum dried over night at 70 °C. The weight per unit area and the geometry of the samples are used to calculate the reference values for the fibre volume content. After that the sample pieces are, like the calibration standards, pulverized, dried again and their fibre volume content calculated based on the average values of the total carbon content.

Results and discussion

In the present paper the determination of the natural fibre content in an NFRP laminate is derived from the calculation of the total carbon content by means of chemical analysis. This method presupposes that the carbon contents of the natural fibre and the biopolymer are different. This condition is fulfilled due to their different chemical families. The natural fibres are a cellulose structure corresponding to a polysaccharide. In contrast, the biopolymer is a derivatized fatty acid ester (linseed-oil acrylate) (see Fig. 1 and Table 1). Another precondition for quantifying the fibre content is the absence of moisture in the test material. For this reason the samples are dried in vacuum to a constant weight. The loss of moisture was 2–4 wt%. The remaining residual moisture can be disregarded.

The determination of the fibre weight content in the laminates is derived from the analysis of the total carbon. This is done by calculating a calibration line, i.e. mix standards are prepared from the pulverized and dried natural fibre material and the biopolymer resin, and then analysed. Figure 2 shows the calculated calibration line; this is referred to in the subsequent evaluations. The very good calibration line's coefficient of determination ($R^2 = 0.9995$) and the small standard deviation (±1%) demonstrate the high reproducibility of this method.

The analysis results for the NFRP laminates produced with 25 and 50 vol.% natural fibre content are summarized

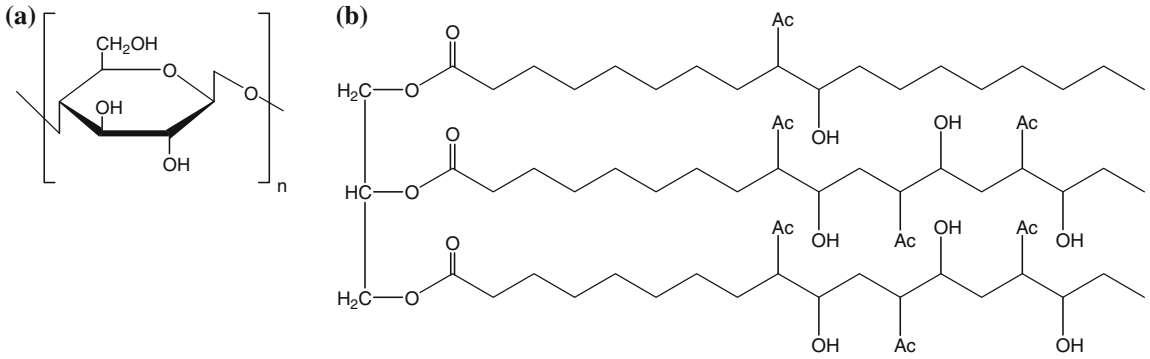

Fig. 1 Structure formula of celluose (**a**) and of linseed-oil acrylate (**b**). Ac: $CH_2CHCOO–$

Table 1 Results of the determination of natural fibre content in NFRP laminates given by ultimate analysis

Samples[a]	Carbon content[d] (wt%)	References calculated by sample geometry		Calculation by ultimate analysis	
		Fibre mass content (%)	Fibre volume content (%)	Fibre mass content (%)	Fibre volume content (%)
Fibre[b]	43.90	–	–	–	–
Matrix[c]	60.91	–	–	–	–
PK-25-1	54.88	34.25	25.76	35.34	26.59
PK-25-3	54.67	35.19	25.74	36.57	26.74
PK-25-5	54.92	35.62	26.32	35.11	25.95
PK-50-1	50.54	61.61	49.02	60.82	48.39
PK-50-3	50.55	60.80	49.19	60.76	49.16
PK-50-5	50.51	59.87	49.32	61.00	50.25

[a] Vacuum dried samples

[b] Non-woven material of hemp/flax (25/75): $\rho = 1.5$ g/cm^3

[c] Biopolymer: $\rho = 1.19$ g/cm^3

[d] Average values of carbon content

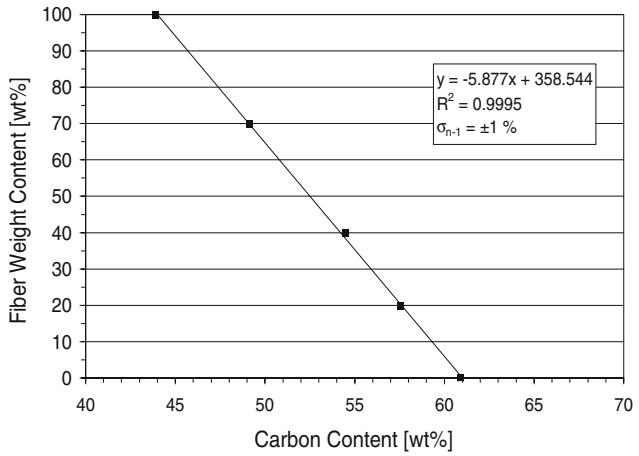

Fig. 2 Calibration line based on mix standards of hemp/flax and a biopolymer resin for the determination of the fibre weight content in natural fibre-reinforced composites (NFRP). Analysis technique: total carbon content by ultimate analysis

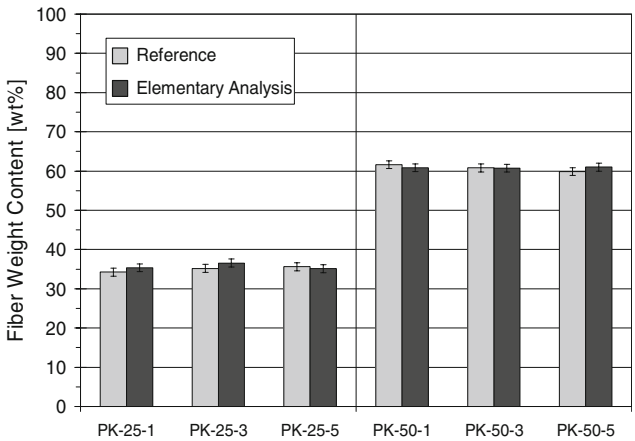

Fig. 3 Fibre weight content of two test series of natural fibre-reinforced composites (NFRP). Comparison of reference data and data obtained from ultimate analysis

in Table 1 and depicted in Figs. 3 and 4. The total carbon content of each sample is confirmed by repeating the measurements three times. The corresponding fibre weight contents are determined using the calibration line of Fig. 2 and converted into the relevant fibre volume contents using the formula:

$$\varphi_P = \frac{m_P \cdot w_F}{A_P \cdot \rho_F \cdot d_P}$$

φ_P Fibre volume content of test specimen (%)
m_P Weight of NFRP test specimen (g)
w_F Fibre weight content of NFRP test specimen (%)
A_P Surface area of test specimen (cm^2)

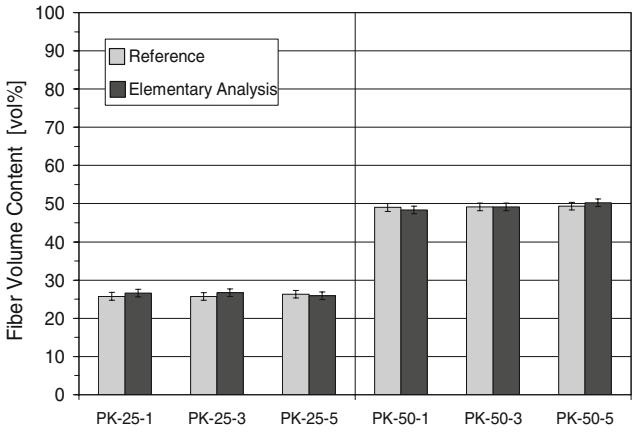

Fig. 4 Fibre volume content of two test series of natural fibre-reinforced composites (NFRP). Comparison of reference data and data obtained from ultimate analysis

ρ_F Density of natural fibre (g/cm^3)
d_P Thickness of test specimen (cm)

The absolute fibre weight contents and the fibre volume contents of the NFRP laminates are used as reference values. These are calculated from the weight per unit area and the geometry of the samples. The good correlation between the fibre volume contents determined from the ultimate analysis and the calculated reference values shows the reliability of this new measurement method. The standard deviation is ±1%.

This new analysis method can be used to determine fibre volume contents in NFRP laminates quite simply and cost effectively and with high reproducibility. In particular, statements can be made about the homogeneity of the fibre distribution over the total area of the composite part, which can vary greatly due to the different drapability of the fibre semi-finished products. This method could represent a good analysis technique for quality-controlled manufacturing, and it should be possible to apply it to most natural fibre composites. The only requirement for the approach is a sufficient difference in the carbon contents of the natural fibre and the biopolymer, because the total carbon is calculated as a sum parameter.

Summary and conclusion

The present paper illustrates a new simple and cost-efficient method for the determination of fibre volume content in NFRP with good reproducibility. The measurement of the fibre content is attributed to the quantification of the total carbon content of the composite by ultimate analysis. The differentiation of resin matrix and natural fibre is possible on account of the different carbon contents of both components. In this way the fibre volume content of porous and also compact fibre composite parts can be calculated. Precondition to the application of ultimate analysis is the absence of water in the composite materials so that a good pre-drying must be carried out before the measurement. The fibre volume content is measured by this method with a standard deviation of ±1%.

References

1. Witten E (2008) In: Manual of the 11th international AVK conference, Essen, Germany
2. Liu Z, Erhan SZ, Akin DE, Barton FE (2006) J Agric Food Chem 54:2134
3. Larbig H, Scherzer H, Sahike B, Poltrock R (1998) J Cell Plastics 34:361
4. Bledzki AK, Gassan J (1999) Prog Polym Sci 24:221
5. Hornsby PR, Hinrichsen E, Tarverdi K (1997) J Mater Sci 32:443. doi:10.1023/A:1018521920738
6. Hornsby PR, Hinrichsen E, Tarverdi K (1997) J Mater Sci 32:1009. doi:10.1023/A:1018578322498
7. Jiang L, Hinrichsen G (1999) Die Angewandte Makromolekulare Chemie 268:13
8. ASTM D 3171-76, 1990
9. Barton FE, Akin DE, Morrison WH, Ulrich A, Archibald D (2002) J Agric Food Chem 50:7576
10. Fink HP, Bohn A, Pinnow M, Kunze J (2004) In: 5th global wood and natural fibre composites symposium, Kassel Germany, 27–28 April 2004