PROCESSING AND MECHANICAL PROPERTIES OF BIODEGRADABLE STARCH-BASED RESIN REINFORCED WITH NATURAL MINERAL FIBRES

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Abstract

Environmental problems caused by extensive use of plastic polymers arise mainly due to lack of landfill space and depletion of finite natural resources of fossil raw materials like petroleum or natural gas. The substitution of synthetic petroleum-based resins by natural biodegradable resins appears to be one appropriate measure to improve the above-mentioned environmental problems. This study presents the development of a composite that uses environmentally degradable starch-based resin as matrix and natural mineral basalt fibres as reinforcement, and investigates the composite's mechanical properties. Prepreg-sheets were manufactured by means of a modified doctor blade system and hot power press. The sheets were used to manufacture specimens with fibre fractures with volumes ranging from 33 % to 50 %. Specimens were tested for tensile strength, flexural strength and inter-laminar shear strength.

1 Introduction

Many severe environmental issues arise due to extensive use of plastic. The most important characteristics of plastic, durability and light weight, change into severe drawbacks after disposal. If dumped into a landfill, plastic doesn't decompose and lose volume. As a result, the ground remains unstable and further use becomes difficult if not impossible. If plastic is burnt at a waste incineration plant, high energy consumption and the dispersal of harmful substances are only two of the many consequences. The burning of plastic reinforced with glass fibres may even cause damage of the incinerator kiln. The depletion of finite natural petrochemical resources, acceleration of the greenhouse effect, emission of toxic gases and damage to wildlife and marine species additionally accompany the waste production process.

In an attempt to resolve these issues while creating an alternative for composites reinforced with synthetic fibres, research on 'green' composites has been conducted since at least the mid-1990s worldwide.

'Green' composites are defined as materials composed wholly, or in part, of constituents which descend from renewable resources. This definition applies to both the reinforcement and matrix phases of the composites [1]. One crucial characteristic, which is common to most natural constituents used in green composites, is biodegradability. Biodegradable composites are composed of biodegradable polymers and natural fibres in the majority of cases. Advantages of biodegradable composites include: complete biological degradation, reduction in the volume of garbage, compostability in the natural cycle, preservation of fossil-based raw materials and protection of climate through reduction of carbon dioxide emission [2].

Natural fibres can be classified in several categories (Fig. 1). Most fibres that are currently used for manufacturing of green composites are cellulose-based plant fibres. Although cellulose-based fibres possess several advantages, including low cost, low density, high specific properties and biodegradability, they exhibit some severe drawbacks. Some disadvantages of natural fibres are moisture absorption leading to fibre swelling, low thermal resistance, local or seasonal variations in quality, anisotropic fibre properties and low compressive as well as transverse strength [3].

Taking these drawbacks into account and considering that it has been demonstrated that the

greatest impact in environmental terms arises from the polymer matrix, usually derived from petrochemical resources, rather than from the reinforcement fibre [1], we have chosen to use environmentally degradable starch-based resin as matrix and natural mineral basalt fibres as reinforcement, and investigated in this study the composite's mechanical properties depending on modifications to the processing method and on variation of the fibre volume fraction.

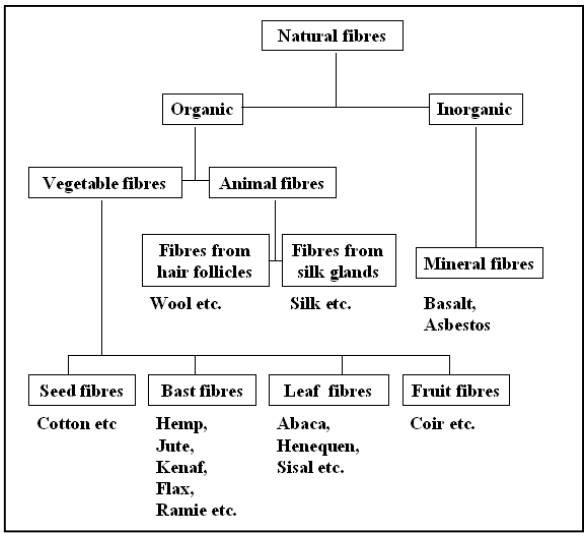

Fig. 1. Classification of natural fibres [4]

2 Materials

2.1 Resin

A biodegradable emulsion type starch-based resin made mainly of maize (Landy CP-300, Miyoshi Yushi Inc.) was used as matrix resin. Fine resin particles of approximately 5 μm in diameter, which consist mainly of starch fatty acid ester and aliphatic polyester, are dispersed in a water-based solution. Properties of CP-300 are shown in Table 1.

Table 1. Properties of starch resin CP-300 [5]

Density [g/cm³]	1.17
Softening point [°C]	57
Minimum film forming temperature [°C]	150
Tensile strength [MPa]	8.9
Tensile elongation [%]	550
Modulus of elasticity [MPa]	430

Starch is an energy storage material occurring as granules in some plants and microorganisms. It is extracted from cereal seeds (maize, wheat, rice), tubers (potato) and roots (tapioca). The heating of starch granules with the use of plasticiser in aqueous media results in gelatinisation caused by irreversible swelling of the granules. This leads to starch solubilisation as amolyse leaches from the granules and amolypectin becomes fully hydrated. As starch products are moisture sensitive and brittle, it is necessary to modify starch or blend it with other materials in order to obtain commercially acceptable thermoplastic starch [6, 7].

2.2 Fibres

Basalt roving (BS-13-1200) with a filament diameter of 13 μ and linear weight of 1200 tex, and plain weave fabric (BT-8) produced by Sudaglass Fiber Technology Inc. (Russia) were used as reinforcement material. The product properties of BT-8 are shown in Table 2.

Table 2. Product properties of basalt plain weave fabric BT-8 [8]

Weight [g/m²]	Thickness [mm]	Warp density [yarns/cm]	Weft density [yarns/cm]
210	0.18	10	8

Mineral basalt fibres possess mechanical properties that are similar or even superior compared to those of glass fibres (Table 3).

Table 3. Comparison of mechanical properties of basalt and glass fibres [8, 9]

Material	Density [g/cm³]	Tensile strength [MPa]	Modulus of elasticity [GPa]	Elongation at break [%]
Basalt	2.80	1850 - 2150	98	3.15
E-Glass	2.54	1850 - 2150	71	4.7

Basalt is a natural substance composed of solidified volcanic lava, and the only ingredient used in the manufacture of basalt fibres. Basalt fibres are made from basalt rocks through a melting process. The basalt rocks can be so finely divided into small particles, that it is possible to form them into fibres. In addition, no additives are used during the basalt production process, which entails additional advantages in costs and environmental terms [9]. Basalt fibre is environmentally and ecologically harmless, and is free of carcinogens and other health hazards [10]. A typical chemical composition of basalt fibres is shown in Table 4.

Table 4. Typical chemical composition of basalt fibres [11]

Element	%
SiO_2	58.7
Al_2O_3	17.2
Fe_2O_3	10.3
MgO	3.82
CaO	8.04
Na_2O	3.34
K_2O	0.82
TiO_2	1.16
P_2O_5	0.28
MnO	0.16
Cr_2O_3	0.06

3 Processing and experimental procedure

3.1 Manufacturing process

The manufacturing process combines the use of two kinds of processing equipment. Prepreg sheets are manufactured during the first processing stage. In order to manufacture the prepreg sheets, we have developed a production process using a doctor blade system (DP-150, Tsugawa Seiki Seisakusho Ltd.) in accordance with [12]. The sheets are subsequently subject to a thermo-mechanical moulding process, in which a hot power press (WF-37, Shinto Co.) comes into operation.

The doctor blade system consists of the doctor blade itself and a ground plate, on which an electric propulsion device feeds a carrier film. The doctor blade consists of two blades, the primary and the secondary blades, which can be independently adjusted. Together with a diagonally attached slab, the primary blade forms a reservoir for the resin (see Fig.2).

Fibres, attached to a carrier film, are fed on the ground plate at a carrier speed of 30 cm/min. They pass beneath the two blades, while resin-emulsion is poured into the reservoir (Fig. 3.).

After drying for 24 h and cutting to size, the preliminary sheets were subjected to an initial pressure and heat applying process (prepreg moulding), turning them into prepreg-sheets (Fig. 4). Afterwards, several layers of prepreg-sheets were stacked and subjected again to a pressure and heat applying process (sample moulding), using a hot power press. Spacers were used during sample moulding to achieve a predefined sample thickness.

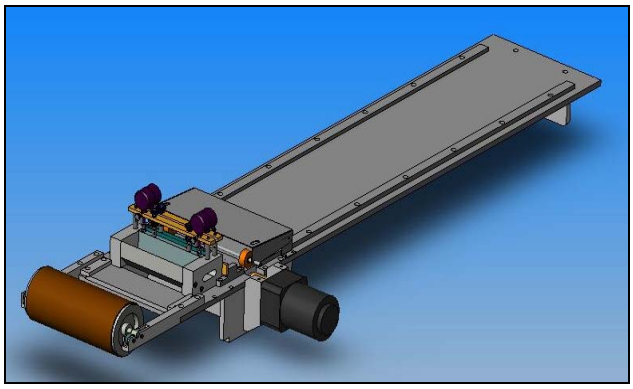

Fig. 2. Doctor blade system (CAD-drawing)

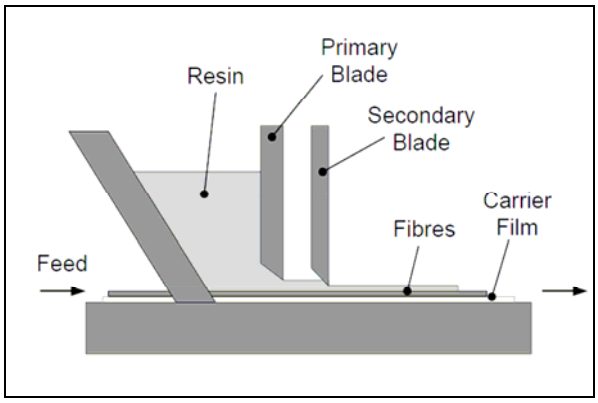

Fig. 3. Doctor blade system (side view)

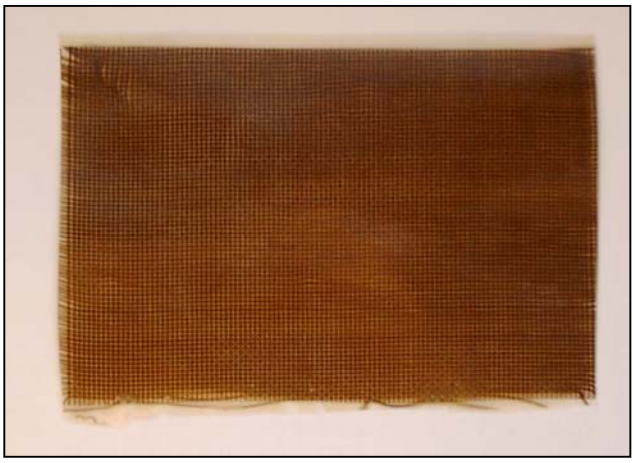

Fig. 4. Basalt fabric reinforced prepreg-sheet sample

The specifications and parameters for the moulding procedure were decided upon after extensive literature review of the existing moulding methods for similar resin systems [13, 14]. The initial processing scheme was identical for both

moulding processes. After putting the sheets onto the lower plunger of the hot press, the heating device was engaged and the sheets heated until they reached a processing temperature of 150°C. Marginal pressure was then applied for 30 minutes to enable the trapped air to escape and to facilitate the impregnation of the matrix among the fibres. The pressure was subsequently increased to 4.9 MPa, while the heating device was switched off, allowing the sample to cool to room temperature, at the rate of approximately 0.5°C/min.

Unidirectional samples were manufactured using basalt roving and textile composite samples were manufactured using basalt plain weave fabric. After producing unidirectional samples with the initial processing parameters, the temperature and pressure for the prepreg moulding process were changed to 130°C and 170°C, and to 9.8 MPa, respectively, in order to determine the influence of the prepreg moulding processing parameters on the properties of the final specimens. The fibre volume fraction of the unidirectional samples was kept constant at 40%.

In order to determine the influence of the volume fibre fraction on the mechanical properties, textile composite samples were produced with 4, 5 and 6 prepreg-sheets, which resulted in fibre fractions by volume of 33%, 38% and 50% respectively. Samples made of 4 prepreg-sheets were tested for tensile properties in 0° and 90° directions, as the properties of the basalt fabric are different for warp and weft directions. All textile composite samples were manufactured with a temperature of 150°C and a pressure of 4.9 MPa in both processing stages. Processing parameters are summarised in Table 5.

Table 5. Processing parameters

Fibre type	Basalt roving (BS-13-1200)	Basalt fabric (BT-8)
Prepreg moulding pressure [MPa]	130, 150, 170	150
Prepreg moulding temperature [°C]	4.9, 9.8	4.9
Sample moulding pressure [MPa]	150	150
Sample moulding temperature [°C]	4.9	4.9
Fibre volume fraction [%]	40	33, 38, 50
Tensile test loading direction [°]	0	0, 90

3.2 Determination of tensile properties

An Instron universal material-testing machine, model 4200, was used for the tension tests. The tests were carried out according to JIS K 7113 with a displacement rate of 1.0 mm/min. All samples had a length of 200 mm, a width of 10 mm and a thickness of 1 mm. End tabs with chamfered edges, manufactured of cross-plied glass fibre reinforced epoxy resin, were attached to the specimens using an appropriate adhesive, to avoid untimely rupture at the load transmission points (Fig. 5).

During the tests the initiated load was recorded by the attached computer system, while the tensile strain was quantified by means of strain gauges.

Fig. 5. Tension test setting

3.3 Determination of flexural properties

A Shimadzu AGS-1000B universal material-testing machine was used for the flexural tests. The tests were carried out according to JIS K 7017 as 3-point-bending tests, with a displacement rate of 1.0 mm/min. Samples had a length of 100 mm, a width of 15 mm and a thickness of 2 mm.

During the tests the initiated load was recorded by the attached computer system; the flexural strain was quantified by means of strain gauges.

3.4 Determination of interlaminar shear strength

Apparent interlaminar shear strength was determined, according to JIS K 7057 standard, using the short beam method with a Shimadzu AGS-1000B universal material-testing machine. Samples had a length of 20 mm, a width of 10 mm and a thickness of 2 mm. The displacement rate was set at 1 mm/min.

4 Test Results

4.1 Mechanical properties of unidirectional reinforced composite

Samples manufactured with the initial prepreg moulding parameters of 150°C and 4.9 MPa were tested for tensile strength, bending strength and interlaminar shear strength. The results are summarised in Table 6.

Table 6. Mechanical properties of unidirectional reinforced composite

Prepreg moulding pressure [MPa]	4.9
Prepreg moulding temperature [°C]	150
Fibre volume fraction [%]	40
Tensile strength [MPa]	517
Elongation at break [%]	2.0
Modulus of elasticity [GPa]	31.8
Flexural strength [MPa]	236
Flexural modulus [GPa]	22.6
Interlaminar shear strength [MPa]	7.9

In the case of continuous fibre reinforced composites, the tensile strength σ_{1c} can be predicted using the rule of mixture according to [15]

$$\sigma_{1c} = (1-V_f)\sigma_{1m} + V_f\sigma_{1f} \qquad (1)$$

while the modulus of elasticity can be displayed using the following equation

$$E_{1c} = E_f[(1-V_f)\sigma_{1m}/\sigma_{1f} + V_f] \qquad (2)$$

where σ and E indicate stress and modulus of elasticity, respectively. V_f is the fibre volume fraction and indices c, m and f refer to composite, matrix and fibre, respectively.

The predicted tensile strength and the modulus of elasticity for the unidirectional composite laminae were 745.3 MPa and 35.9 GPa respectively. While the actual value of the elasticity of modulus was almost equal to the predicted one, the actual tensile strength showed only 69% of the predicted value.

Although fibres can be oriented parallel to external tensile loads, it is almost impossible to avoid transverse stresses, which present a major problem in unidirectional laminae. Transverse stresses in unidirectional laminates may lead to premature failure, due to relatively small matrix-dependent transversal strength and stiffness.

All unidirectional composite samples in this study were produced by aligning basalt roving by hand. As the fibre orientation is not completely parallel, the possibility of premature failure increased. As a result the unidirectional composite specimens were fractured by premature matrix failure as can be seen in Fig. 6.

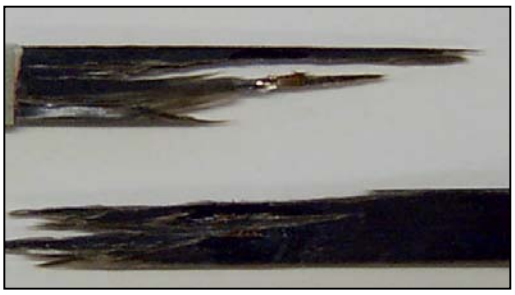

Fig. 6. Fractural behaviour of unidirectional composite

An important attribute of the rule of mixtures is the assumption for a strong fibre-matrix bond. As it is apparent by the low value of the interlaminar shear strength of only 7.9 MPa, the adhesion between the laminae and between fibres and matrix in the interlaminar area is not sufficient. This low value further promotes a premature matrix failure. The fibre debonding in the interlaminar area is visible in the SEM micrograph of the interlaminar fracture surface (Fig.7.)

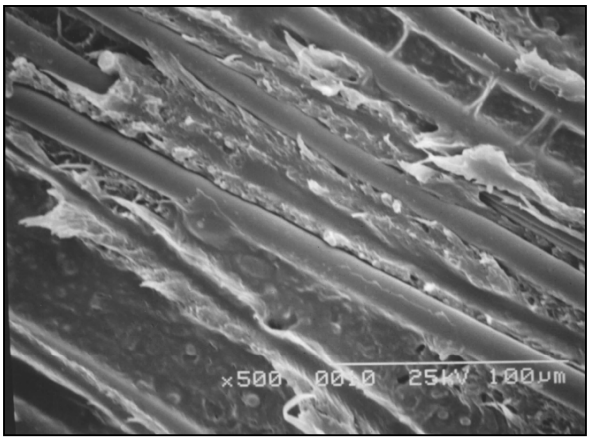

Fig.7. SEM-micrograph of the interlaminar fracture surface

The effect of the processing temperature on the mechanical properties of the unidirectional composite is shown in Fig.8. The tensile strength and the modulus of elasticity increased by means of a processing temperature increase from 130°C to 150°C. This may be attributed to better fibre wetting through higher resin viscosity. A further

increase of the processing temperature to 170°C led to a decrease in the tensile strength, suggesting possible damage to the resin matrix, due to high temperature.

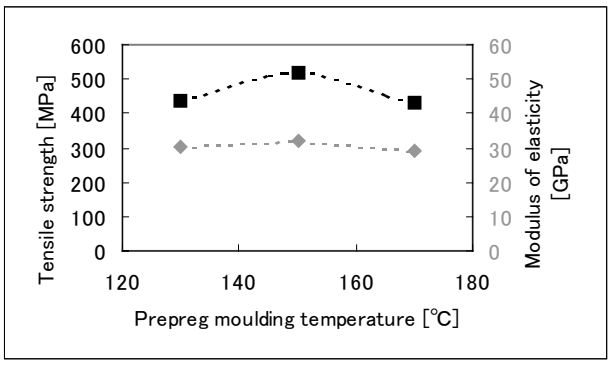

Fig. 8. Effect of processing temperature on the mechanical properties

The effect of the processing pressure on the mechanical properties of the unidirectional composite is shown in Fig.9. An increase in processing pressure from 4.9 MPa to 9.8 MPa led to a decrease in tensile strength, which may be caused by increased misalignment of the fibres in the loading direction.

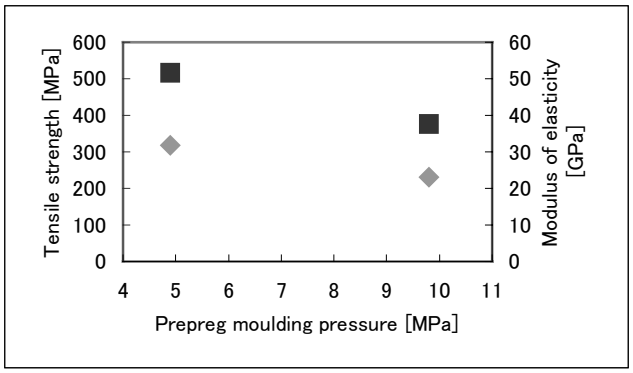

Fig. 9. Effect of processing pressure on the mechanical properties

4.1 Tensile properties of woven textile-reinforced cross-ply composite

Composite textile samples with a volume fraction of 33% were tested for tensile strength in the warp and weft directions. They displayed an average tensile strength of 242 MPa and 281 MPa, respectively. The values of the modulus of elasticity were 10.3 GPa and 11.8 GPa, respectively.

According to [15], the final fracture strength of a cross-ply laminate is determined by the fracture strength of the longitudinal layers and is given by

$$\sigma_c = \sigma_{II} b/(d+b) \qquad (3)$$

where σ_{II} is the stress parallel to the tensile loading direction, b the fraction of the fibres in the loading direction and d the fraction of the fibres in the transversal direction.

The actual tensile strengths of the samples with a fibre volume fraction of 33% were almost equal to the predicted values. An increase in the fibre volume fraction led to an increase in tensile strength, but the tensile strength values for V_f = 38% and V_f = 50% only reached 77% and 71% of the predicted values, as shown in Fig. 10, where the dotted line shows the predicted tensile strength values.

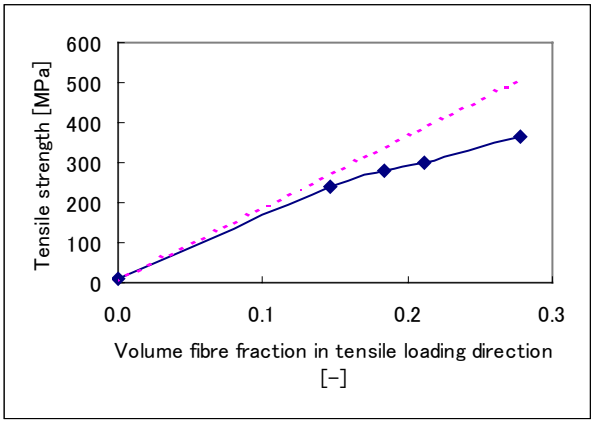

Fig. 10. Relation between tensile strength and fibre volume content

The decrease of the actual tensile strength compared to the rule of mixture values can be explained by non-sufficient fibre wetting at higher volume fractions. Comparing the fracture behaviour of a 33%-sample and a 50%-sample, it is evident, that the former shows an almost linear fracture surface, while the later exhibits a rather brush-like appearance, which suggests an increased fibre pull-out (Fig. 11).

A further indicator for a decreased fibre wetting and a decreased fibre-resin-bond is the SEM micrograph (Fig. 12) of the fracture surface of the 50%-sample. The resin did not penetrate the fibre bundles sufficiently. A sufficient fibre-matrix-bond only took place partially on the outer fibres of the bundles and the fibres inside the bundles are touching each other. This situation leads to an increase in fibre pull-out.

Fig. 11. Fracture behaviour of cross-ply specimens left: 50 vol-%, right: 33 vol-%

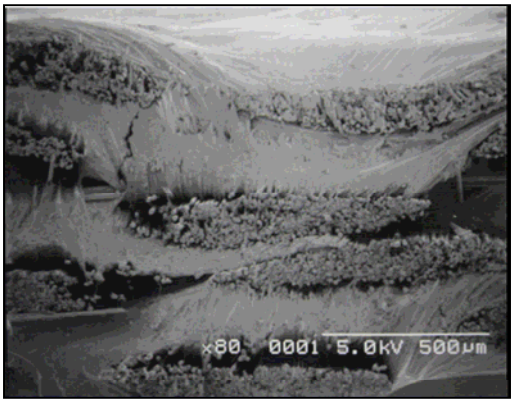

Fig. 12. SEM micrograph of fracture surface of cross-ply composite with 50 vol-% of fibres

5 Conclusions and considerations

(1) By use of basalt roving and plain weave basalt fabric with starch resin, all-natural, high strength, unidirectional 'green' composites and all-natural, high strength, cross-ply 'green' composites have been successfully manufactured, through the utilization of hot press machinery and a doctor blade system.

(2) By applying of the doctor blade system, the fabrication process was successfully automated to a high degree.

(3) Several factors responsible for favourable mechanical properties have been identified and will be considered through further research.

To improve the properties of the unidirectional materials, the use of woven UD fabrics, instead of rovings, should be taken into consideration. The use of surface treatment to improve the fibre-matrix-adhesion will also be investigated. Further improvement of the manufacturing process, as well as consideration of various biodegradable resins, will be the focus of future research in order to improve the mechanical properties of basalt fibre reinforced biodegradable resin.

Although the manufactured composites can be improved, it has been ascertained that, due to their favourable mechanical properties and limited impact on the environment, mineral basalt fibres are a promising alternative as reinforcing agents in 'green' composites.

References

[1] Hughes M. "Applications". *"Green composites: Polymer composites and the environment"*, Ed. by C.Baille, Woodhead Publishing, 2004, pp 233-251.

[2] Sain M., Panthapulakkal, S. "Green fibre thermoplastic composites". *"Green composites: Polymer composites and the environment"*, Ed. by C.Baille, Woodhead Publishing, 2004, pp 181-205.

[3] Stamboulis A., Baille C.A. and Peijs T. "Effects of environmental conditions on mechanical and physical properties of flax fibers". *Composites: Part A*, Vol. 32, pp 1105-1115, 2001.

[4] JIS L 0204-1

[5] Tanaka H., "Denpun emarujon randi". *Engineering Materials*, Vol. 51, No. 3, pp 58-62, 2003. (in Japanese)

[6] Plackett D. "Natural polymer sources". *"Green composites: Polymer composites and the environment"*, Ed. by C.Baille, Woodhead Publishing, 2004, pp 123-153.

[7] Chiou B.S. et. al. "Starch Polymers: Chemistry, Engineering, and Novel Products". *"Natural Fibers, Biopolymers and Biocomposites"*, Ed. by A.K. Mohanty, M. Misra and L.T. Drzal, Taylor & Francis, 2005, pp 639-670.

[8] www.sudaglass.com

[9] www.chubuindustry.co.jp

[10] Kogan F.M., Nikitina O.V., "Solubility of Chrysotile Asbestos and Basalt Fibers in Relation to their Fibrogenic and Carcinogenic Action". *Environmental Health Perspectives*, Vol. 102, Supplement 5, pp 205-206, 1994.

[11] www.albarrie.com

[12] Tanimoto T., "Continous-fibre CMC fabrication by using pre-impregnated sheets", *Composites: Part A* Vol. 30, pp 583-586, 1989.

[13] Ochi S., Takagi H. and Tanaka H. "Development of High-Strength Cross-Ply "Green" Composites". *Zairyo*, Vol. 52, No. 7, pp 857-862, 2003. (in Japanese)

[14] Dauda M., Yoshiba M. "Processing and Mechanical Properties of Long Maize Fiber Reinforced Polypropylene Composites". *Transactions of MRSJ*, Vol. 26, No. 4, pp 1083-1090, 2001.

[15] Hull D. *"An introduction to composite materials"*. Cambridge University Press, 1981.