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Environmentally friendly technologies for new polymer composite materials: challenges and opportunities

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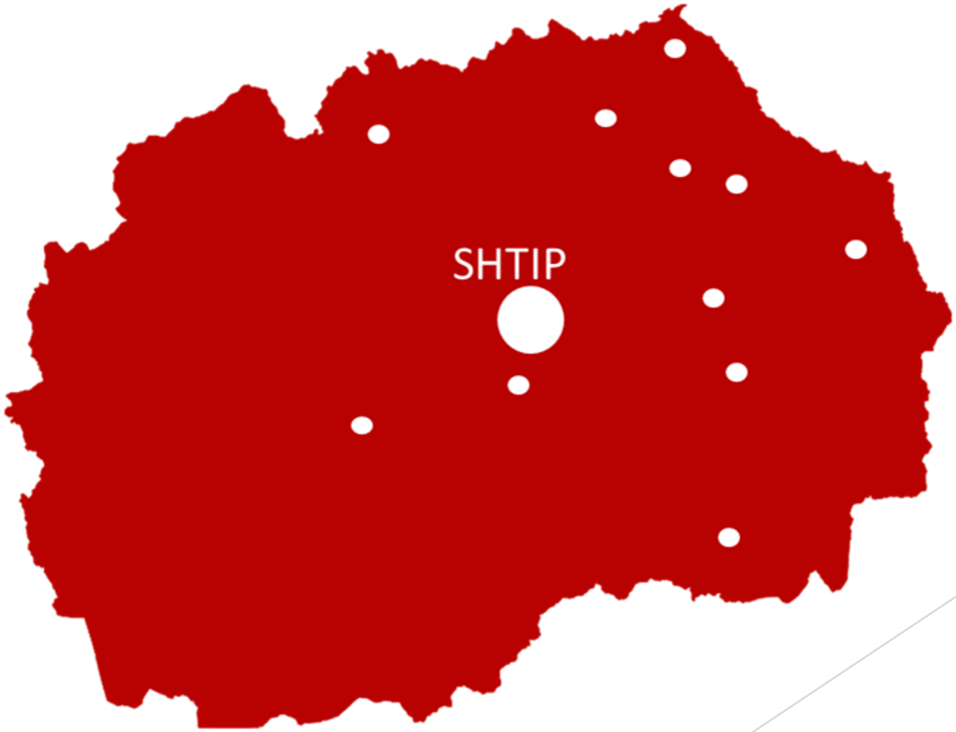
Facts about me

- Associate professor at state University Goce Delcev Shtip, Faculty of Technology

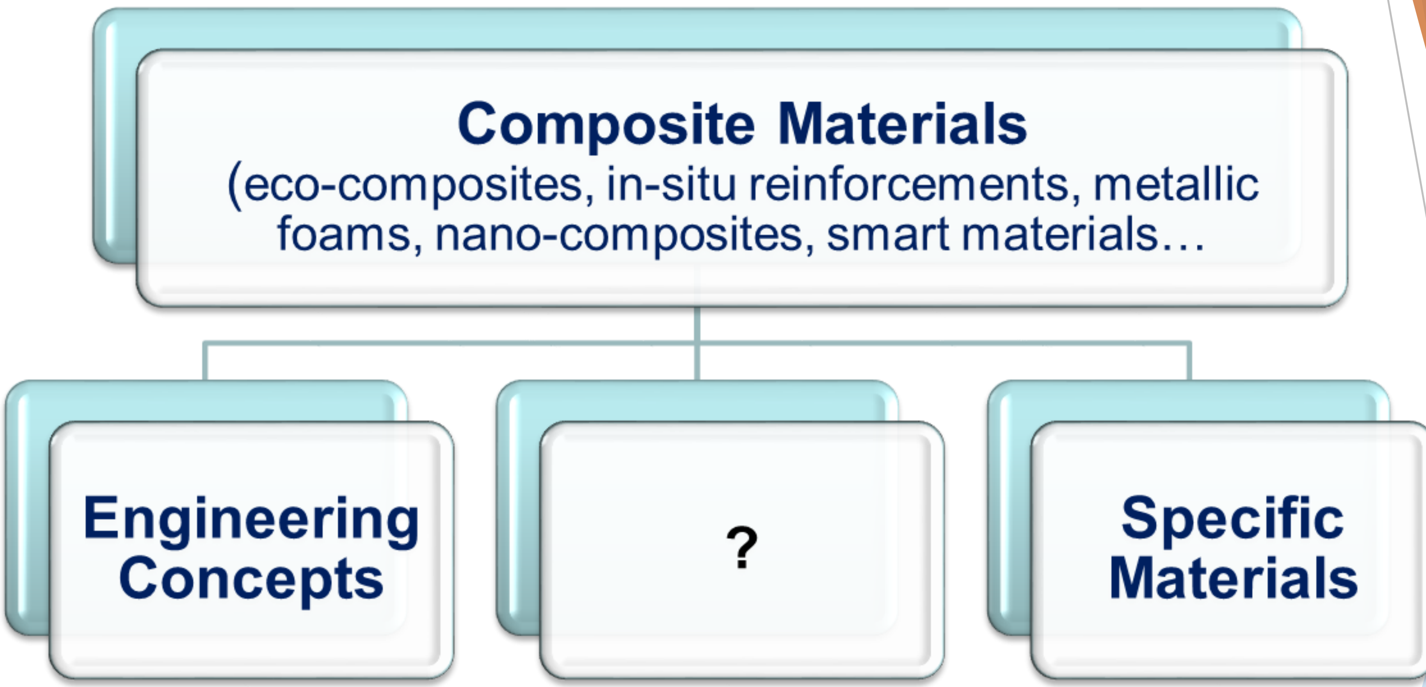
- Field of research: polymer composite materials, eco-composite materials, material development and characterization, thermal characterization of polymeric materials, surface modification of polymers and fibers.



Polymer composites - fibre reinforced polymers

- high performance materials
- for structural applications where high strength-to-weight and stiffness-to-weight ratios are required.
- Requirements - multidisciplinary

Polymer composites



Main focus would be given on composite materials since we can interfere with their structure and tailor their properties in accordance to the end use requirements.

Fibre reinforced plastics: matrices, reinforcements

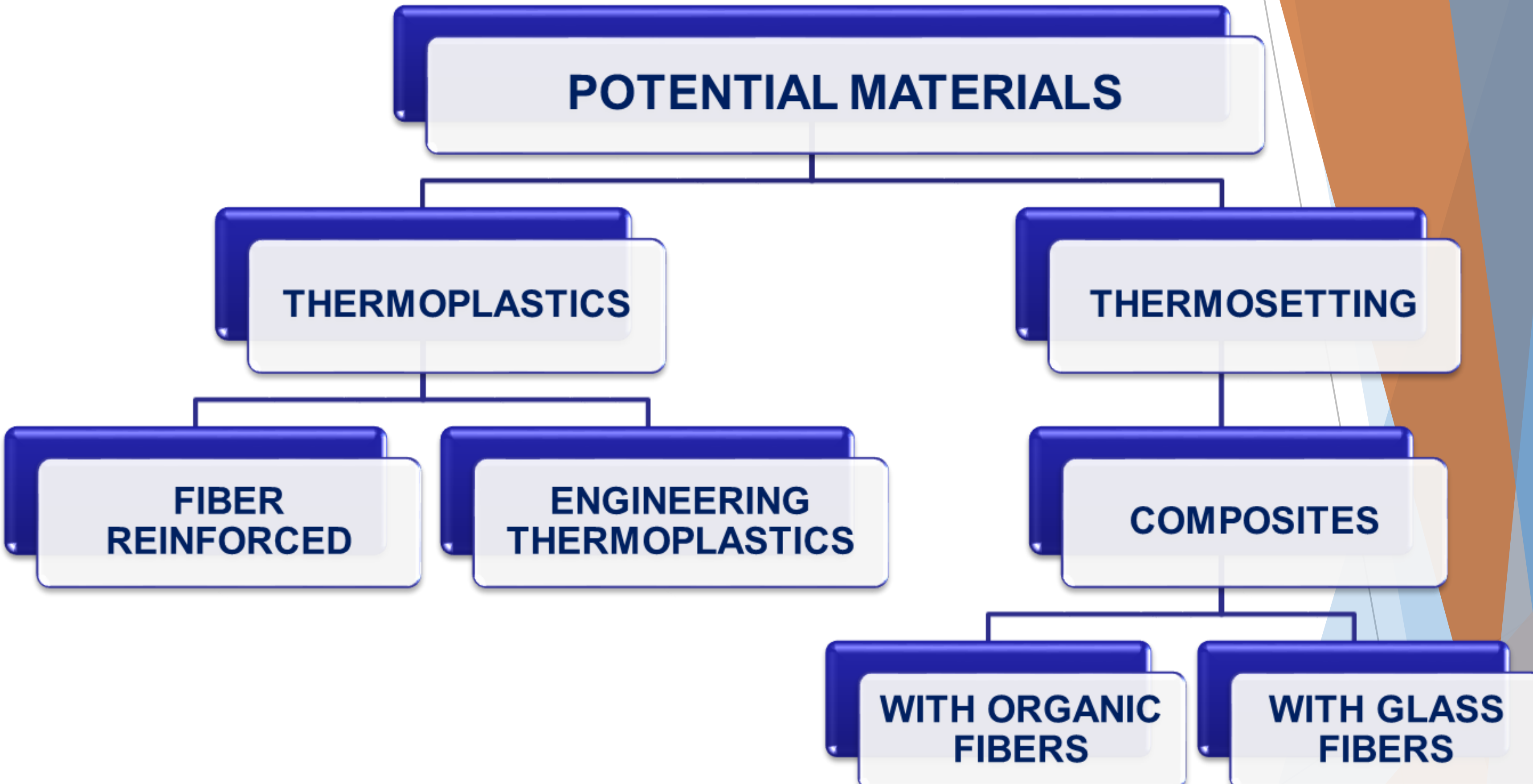
Thermoplastic polymers:

- ✓ *Can be reformed and reshaped by simply cooling and heating,*
- ✓ *flexible and reformable,*
- ✓ *Have lower stiffness and strength*
- ✓ *poor creep resistance at high temperature, and*
- ✓ *Are more susceptible to solvents*

Thermosetting polymers:

- ✓ *Cannot be remelted and reformed.*
- ✓ *Offer high rigidity, thermal and dimensional stability, high electrical, chemical and solvent resistance.*

Fibre reinforced plastics: matrices, reinforcements



Engineering plastics are used "as they are" with no possibility to interfere with their structure i.e. their properties. In fact, all these are commercial products.

Fibre reinforced plastics

- **Research and development - have grown rapidly**
- fibers and matrix materials,
- fabrication process.

- **Advantages over other traditional construction materials:**
- high tensile strength to weight ratio,
- ability to be molded in various shapes.

- **Potential resistance to environmental conditions, resulting in potentially low maintenance cost.**

- **Application in constructions:**
- upgrading existing structures and
- building new ones which can be applied to various types of structures, for example: platforms, buildings and bridges.

Raw materials

Thermosetting resins

- *Epoxy resin for laminating*
- *Epoxy resin for filament winding*
- *Phenolic resin*
- *Vinyl ester*
- *Polyester resin for pultrusion process*

Accelerator for resins
Hardener for resins

Thermoplastic resins

- ***Isostatic Polypropylene (PP)***
- ***Poly lactic acid (PLA)***
- *Polyvinyl butyral (PVB)*
- *Polycarbonate (PC)*
- *Polyethylene (PE)*
- *Nylon*



Raw materials

Fabrics used for laminating

- *Glass, Aramid, Carbon fabric*
- *Woven roving fabric*
- *Cotton fabric*
- *Nonwoven (mat) material*

Rovings used for filament winding

- *Glass*
- *Carbon*
- *Polyester*
- *Aramid*

Natural fibers/fillers

- *Kenaf*
- *Cotton*
- *Rice hulls*
- *Paper*

DRIVING FORCE FOR A NEW GENERATION

***NEW COMPOSITES / ECO-MATERIALS*:**

-Petroleum resources depletion rate
(100.000 times faster than nature can create it)
-Environmental awareness

New natural fiber reinforced composite materials that are compatible with the environment

NEW COMPOSITES ?

Composites: matrices, reinforcements

Eco-friendly; eco-; green; biocomposites

- Natural fibers - reinforcement

- Polymer matrix - thermoplastic recyclable, thermoset, biodegradable, bio-based

<u>Application</u> :

- upgrading existing structures and

- building new ones which can be applied to various types of structures as non bearing materials.

<u>for example</u>: platforms, buildings, interior partition walls, ceilings, flooring, composite structural components with integral thermal and acoustic insulation for improvement of energy efficiency in eco-buildings etc.

NATURAL FIBERS AS REINFORCEMENTS FOR COMPOSITES

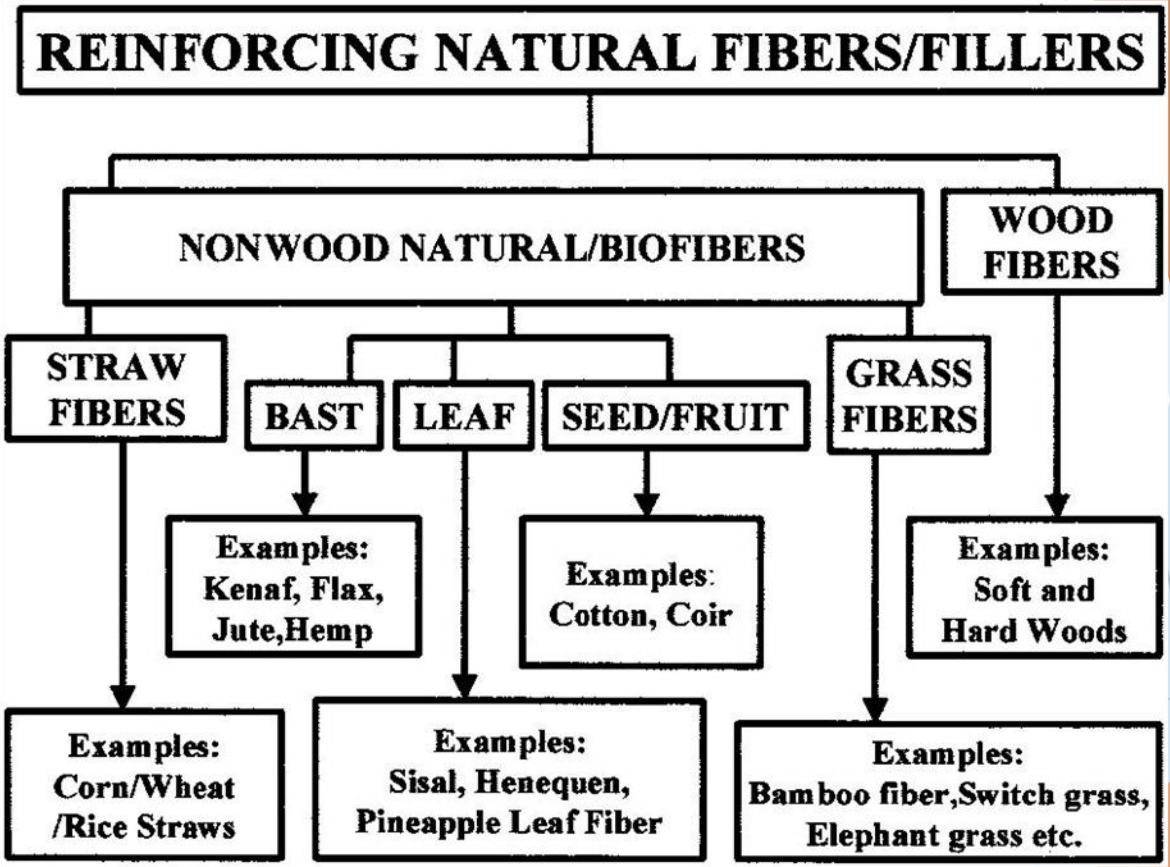
- growing interest in NF reinforced composites
- high performance in terms of mechanical properties, significant processing advantages, chemical resistance, and low cost/low density ratio.
- environmental reasons - increased interest in replacing reinforcement materials (inorganic fillers and fibers) with renewable organic materials.
- brief review of the most commonly used polymers and natural fibers (NFs) in a new group of composite materials.

Commonly used polymers and natural fibers

POLYMERS	NATURAL REINFORCEMENTS
Polyhydroxybutyrates (PHB)	Rice straw
Polyhydroxybutyratevalerate (PHBV)	Hemp
Poly(lactic acid) (PLA)	Jute
Polypropylene (PP)	Sisal
Polyethylenterephtalate (PET)	Cellulose (recycled paper)
	Kenaf

NFs can represent environmentally friendly alternatives to conventional reinforcing fibers (glass, carbon, kevlar)!

RENEWABLE RESOURCES:
NATURAL FIBERS



Dimensions of some natural fibers

Fiber	Average length (mm)	Width (mm)
Cotton	10–60	0.02
Flax	5–60	0.012–0.027
Hemp	5–55	0.025–0.050
Juta	1.5–5	0.02
Straw	1–3.4	0.023
Kenaf	2.6–4	0.018–0.024

- *on their origin,*
- *quality of plants location,*
- *the age of the plant, and*
- *the preconditioning.*

Chemical composition and structural parameters of natural fibers

Fiber	Cellulose (%)	Hemi-cellulose (%)	Lignin (%)	Extractives (%)	Ash (%)	Pectin (%)	Wax (%)	Microfibril/ spiral angle (°)	Moisture content (%)
Jute	61–71	13.6–20.4	12–13	/	/	0.2	0.5	8.0	12.6
Flax	71–78	18.6–20.6	2.2	2.3	1.5	2.2	1.7	10.0	10.0
Hemp	70.2–74.4	17.9–22.4	3.7–5.7	3.6	2.6	0.9	0.8	6.2	10.8
Kenaf	53–57	15–19	5.9–9.3	3.2	4.7	/	/	/	/
Sisal	67–78	10–14.2	8–11	/	1	10	2.0	20.0	11.0
Cotton	82.7	5.7	/	/	/	/	0.6	/	/

Mechanical properties are determined mainly by the cellulose content and microfibrillar angle!

CRYSTAL MODULE OF CELLULOSE I:
E_l=138 GPa

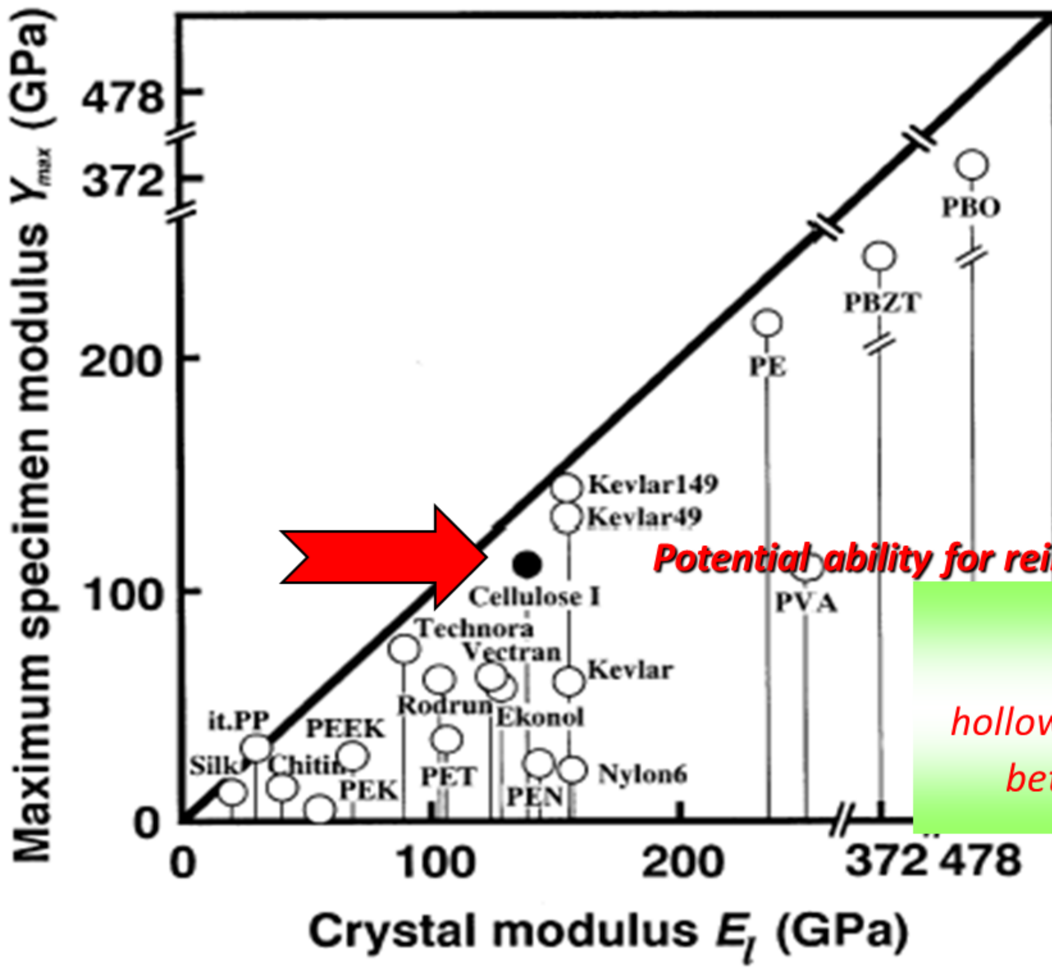


Fig. 2. Relationship between the crystal modulus E_l and the maximum specimen modulus Y_{max} already reported for various polymers.

Additional value:

hollow tubular structure of cell fibers - better noise and heat insulation

Basic properties of some natural fibers

Fiber	Density (g/cm3)	Elongation at break (%)	Fracture stress (MPa)	Young modulus (GPa)
Cotton	1.5	7.0–8.0	287–597	5.5–12.6
Jute	1.3–1.46	1.5–1.8	393–800	10–30
Flax	1.4–1.5	2.7–3.2	345–1500	10–80
Hemp	1.48	1.6	270–900	20–70
Sisal	1.2–1.5	2.0–2.5	511–700	3.0–98
Bamboo	0.8	/	391–1000	48–89
Soft wood	1.5	/	1000,0	40.0

REINFORCING POTENTIAL OF NATURAL FIBERS

Mechanical properties of natural fibers when compared with conventional reinforcements

Fiber	Specific gravity (g/cm3)	Tensile strength (GPa)	Tensile modulus (GPa)	Specific strength (GPa/g cm3)	Specific modulus (GPa/g cm3)
Sisal	1.20	0.08–0.5	3–98	0.07–0.42	3–82
Flax	1.20	2.00	85	1.60	71
E-Glass	2.60	3.50	72	1.35	28
Kevlar	1.44	3.90	131	2.71	91
Carbon (standard)	1.75	3.00	235	1.71	134

- *excellent tensile strength and modulus, high durability, low bulk density, good moldability, and recyclability.*
- advantage over conventional reinforcement fibers in that they are less expensive, available from renewable resources, and have a high specific strength.
- application of long NFs instead of short wood-fibers, such as flax, kenaf, and sisal, is reasonable in architectural and civil works because of the specific modulus, close to that of glass-reinforced composites.

Advantages and disadvantages of reinforcing NF

- low cost,
- high toughness,
- low density,
- good specific strength properties,
- reduced tool wear (nonabrasive to processing equipment),
- enhanced energy recovery,
- CO_2 neutral when burned,
- biodegradability,
- hollow and cellular nature,
- acoustic and thermal insulators,
- exhibit reduced bulk density.

Lack of good *interfacial adhesion*

(cell + lignin + pectin…)

Relatively *low processing temperature*

(below 200°C)

High sensitivity to *humidity*

Low dimensional stability

(swelling, shrinkage)

TREATMENTS/MODIFICATIONS OF NATURAL FIBERS

Research on "a cost-effective" modification of NFs is necessary!

- **Dewaxing (delignification, defatting)**
- **Bleaching**
- **Esterification and etherification**
- **Steam explosion**
- **Graft polymerization**
- **Mercerization (alkali treatment)**
- **Liquid ammonia treatment**
- **Compatibilizers based on novel silane chemistry**
- **Isocyanates**
- **Permanganate treatment**
- **…**

These treatments should not decrease the thermal stability of fiber!

Eco-Houses Based on Eco-Friendly Polymer Composite Construction Materials

Project tasks:

- **Production of eco-friendly polymer composites construction materials** - main task

- Development of natural fiber composites suitable for structural applications.
- Application of various forms of plant fibers: short, long, continuous, woven fabrics and non-woven mats and investigation of their influence on 3P (properties/performance/price) ratio.
- Tailoring of the fiber/matrix interactions and interface characterization.
- Mechanical characterization of the produced composites.
- Development of panelized components with integral thermal and acoustic insulation for improvement of energy efficiency in eco-buildings.
- . . . .

Several kinds of materials were used:

1. SMC

- Kenaf/PP
- Kenaf/biocom
- Kenaf/polyester
- Kenaf/PLA

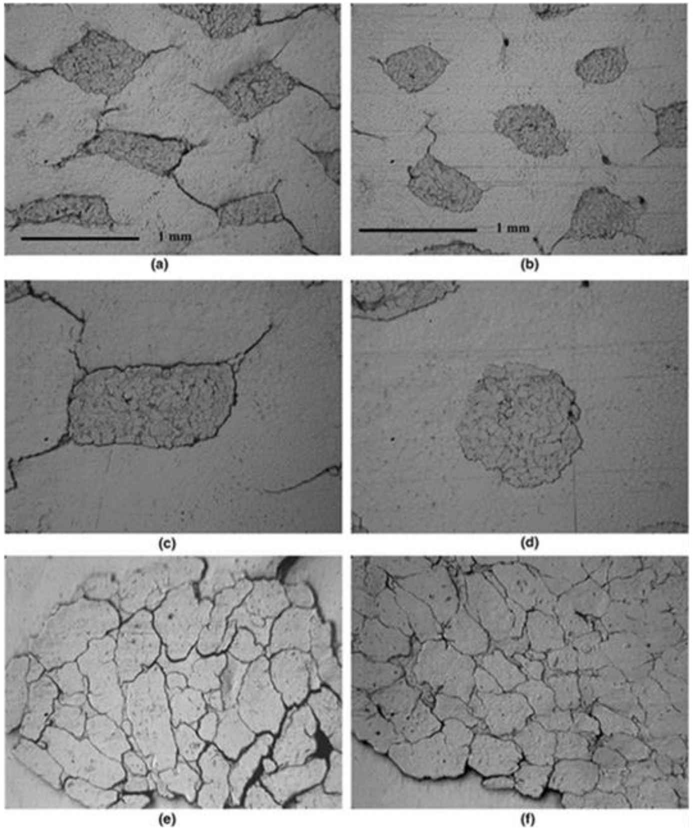
2. Pellets

- Kenaf/PLA
- Rice straw/PLA

Different ratio of the main components + coupling agent

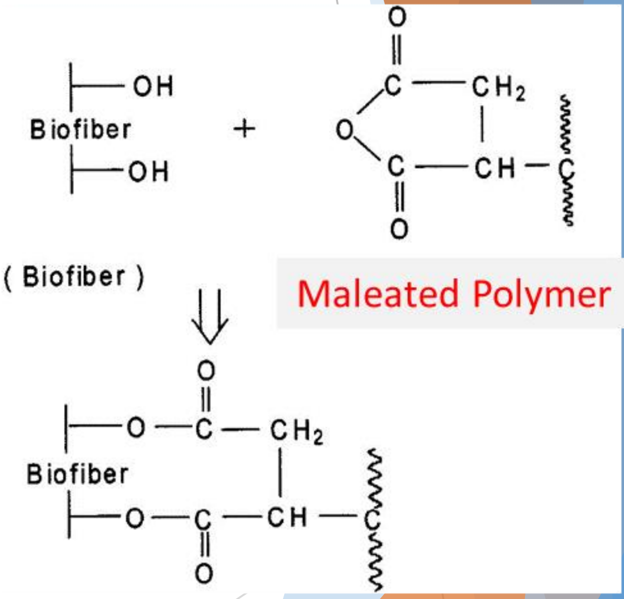
INTERFACIAL ADHESION:
natural fibers embedded in polymer matrix

Fiber/matrix interface region-
key factor determining the load transfer



- *polymer matrix modification (by using compatibilizing agent (CA)*
- *fiber (surface) modification*
- *polymer and fiber modification*
- *processing conditions/new technologies*

FP6 Project ECO-PCCM approach:
PP, PHB, PHBV, PLA modification with MAH-modified polymers

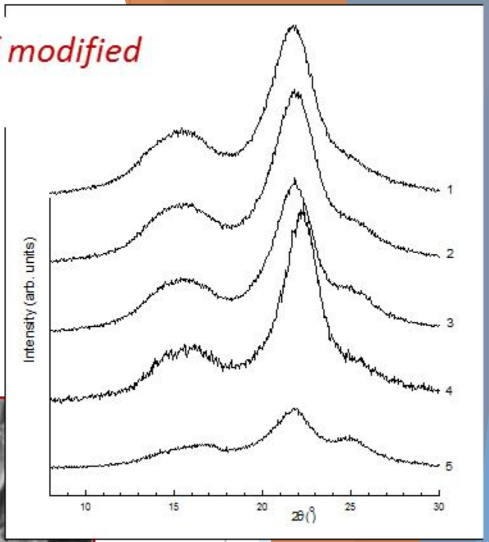


Polymer matrix modification: creation of chemical bonds

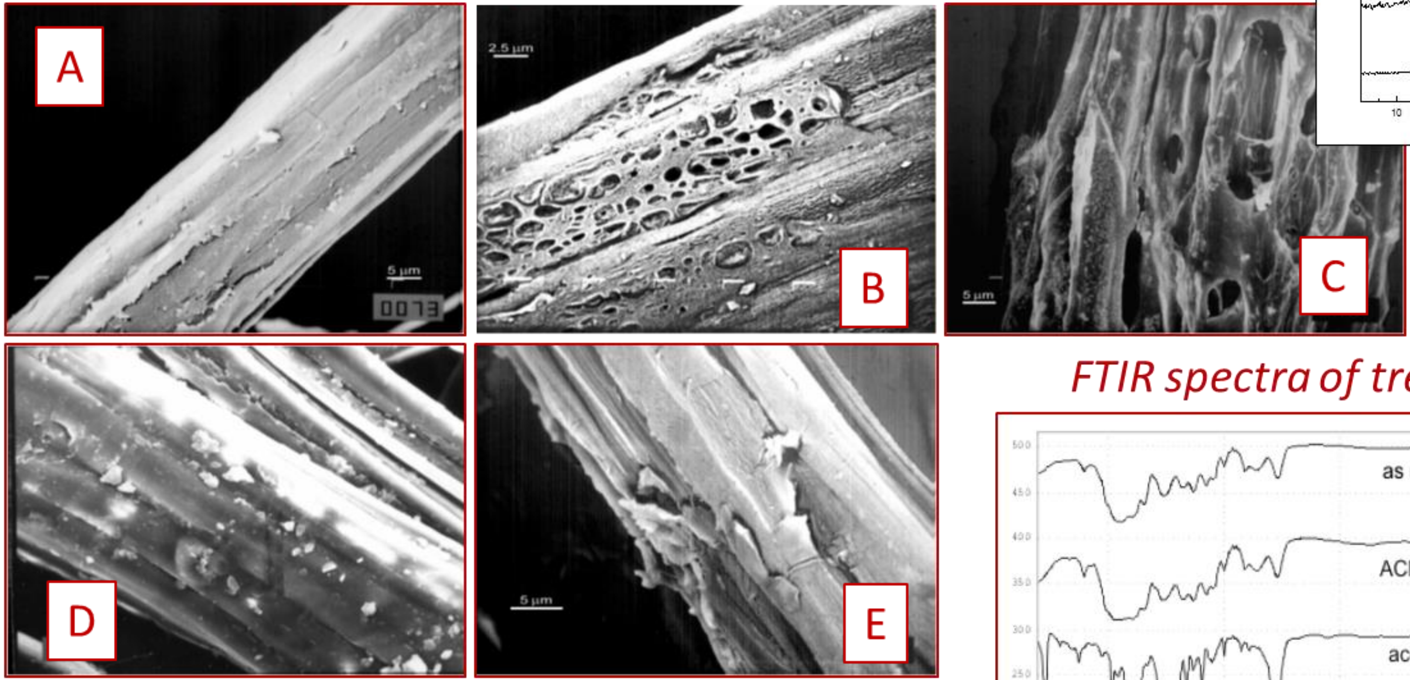
FP6 Project ECO-PCCM:

WAXS analysis, FTIR, SEM of modified kenaf fibers

WAXS patterns of modified kenaf fibers

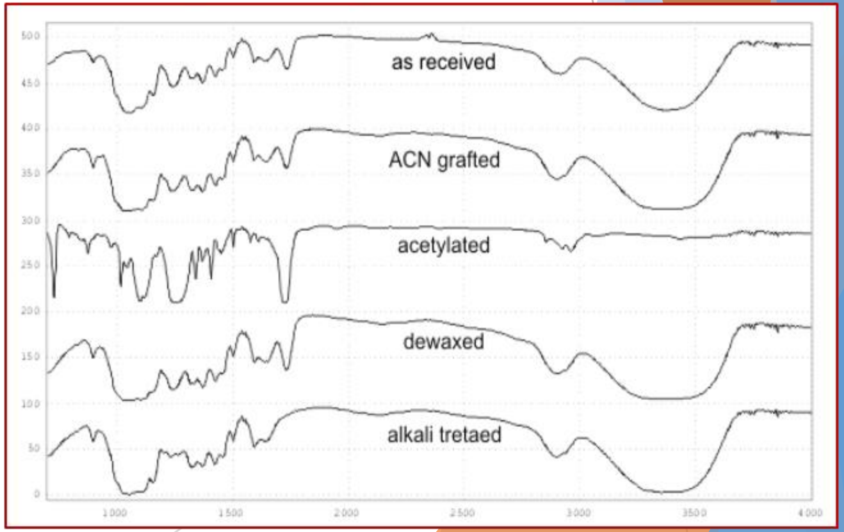


SEM images of kenaf samples



A – As received fiber
B – ACN grafted fiber
C – Acetylated fiber
D – Dewaxed fiber
E –Alkali treated fiber

FTIR spectra of treated kenaf fibres



Codes of composite samples

Codes	Matrix (wt%)		Fiber/Filler		Coupling agent (CA)	
	Type	Content (wt%)	Type	Content (wt%)	Type	Content (wt%)
PP/K/CA	PP	65	Kenaf fibers	30	MAPP	5
PP/RH/CA			Rice Hulls			
PLA/K/CA	PLA	65	Kenaf fibers	30	MAPLA	5
PLA/RH/CA			Rice Hulls			

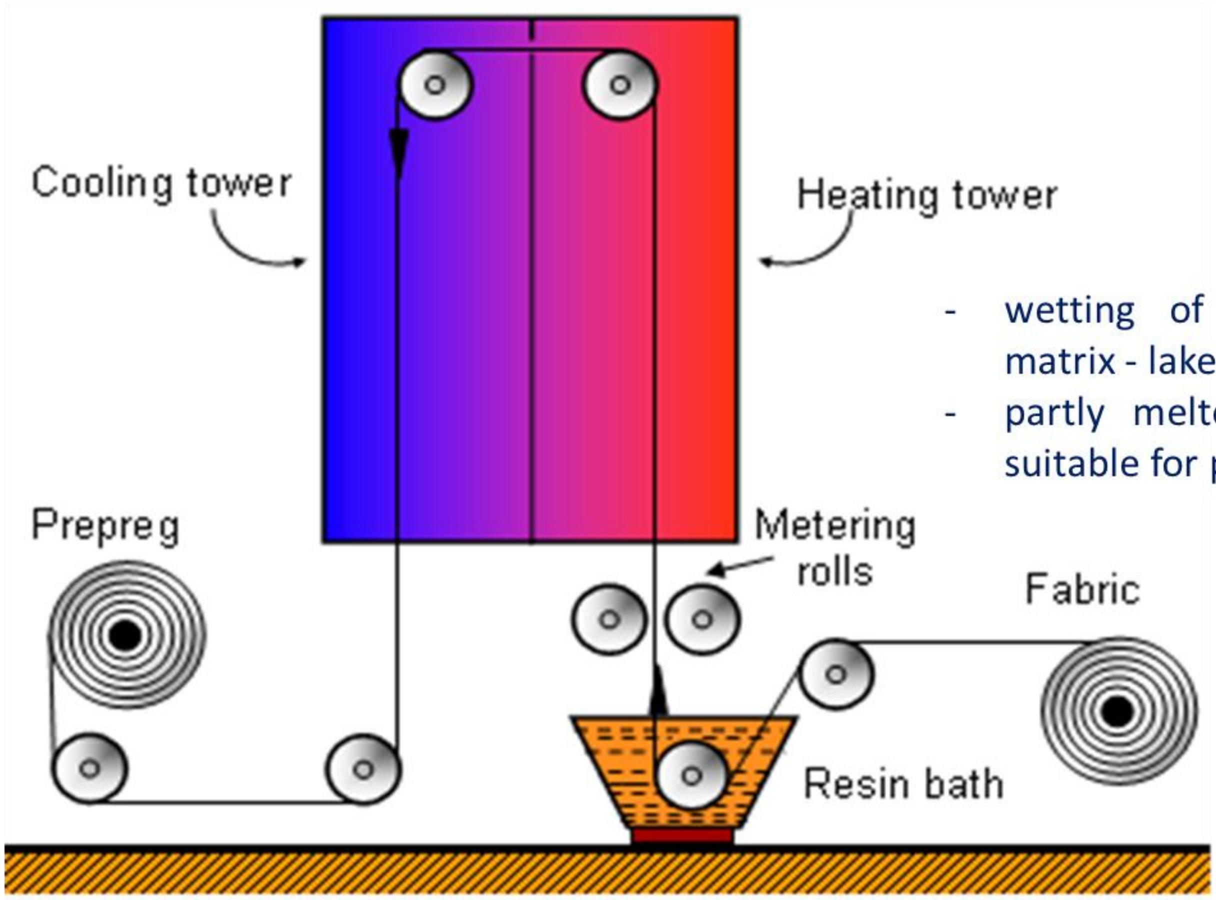
Maleic anhydride-grafted PP (MAPP)
Maleic anhydride-grafted PLA (MAPLA)

were used as coupling agents (CA)

Technology for composite production

- Impregnation – applicable to fabrics only
- Laminating (molding) –applicable to prepregs only
- Filament winding –applicable to rovings only
- **Compression molding – open and close mold**
- **Structural Reaction Injection Molding (SRIM)**
- **Reinforced Reaction Injection Molding (RRIM)**
- **Extrusion**
- **Reactive blending**
- Pultrusion

Impregnation process



- wetting of fibers with the matrix - lake a transparent film
- partly melted and in phase suitable for processing

The final product is **prepreg** (**pre**-im**preg**nated fabric with resin) which is considered a semi-finished product.

Compression molding (CM)

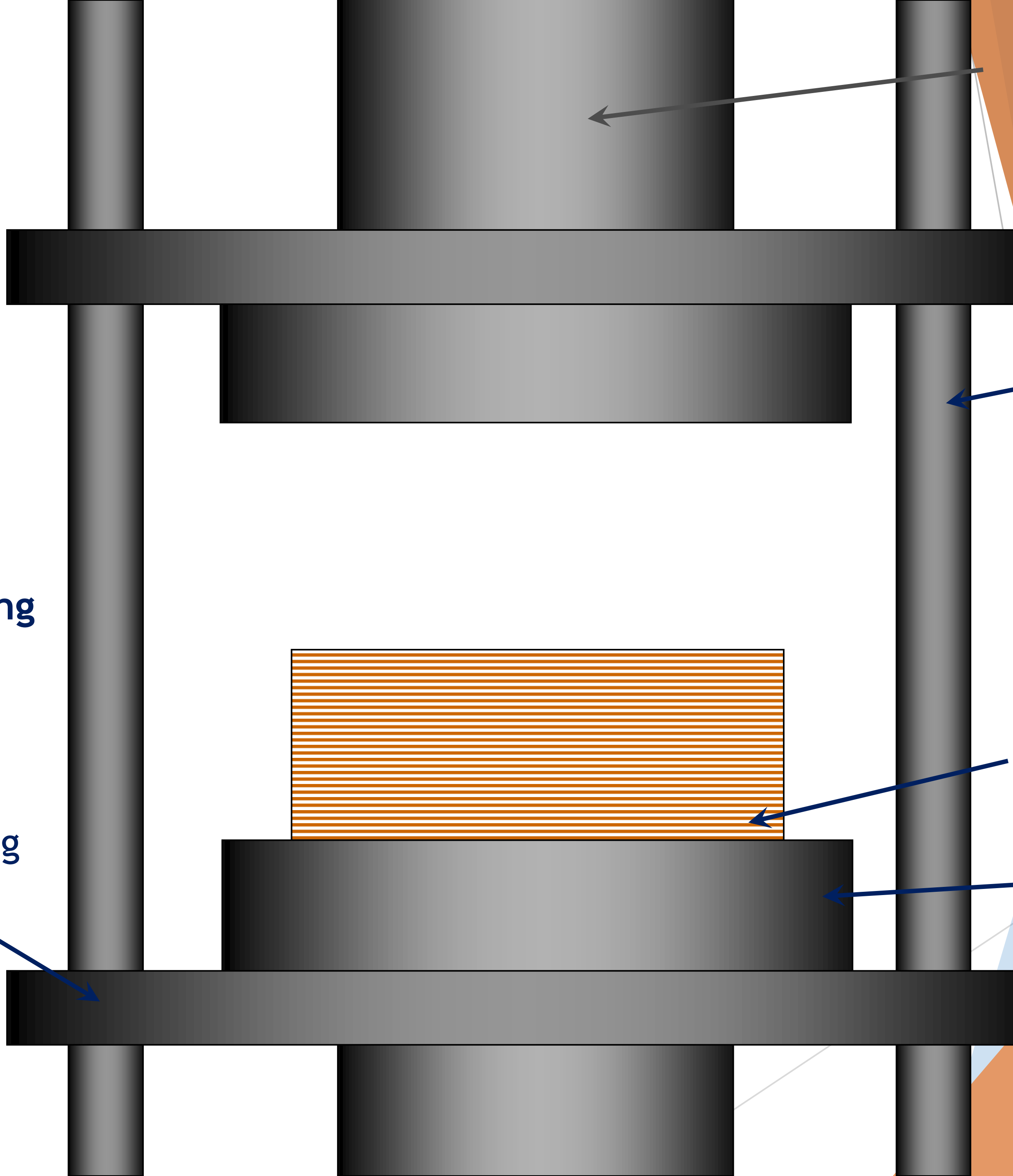
- *major method for processing plastics*
- *high pressure process*
- *applying heat and pressure*
- *in matched or open dies*
- *main processing method for thermoset plastics*
- *also be employed to process thermoplastic materials*
- *compression molding press*
- *composite plate*
- *advantages: short cycle time, high production rate and excellent surface finishes*

Materials used for CM:

- SMC (Sheet Molding Compounds)
- BMC (Bulk Molding Compounds)
- Pellets/granules

Matched die technique

SMC



No mold, single-opening press

FP6 Project ECO-PCCM:

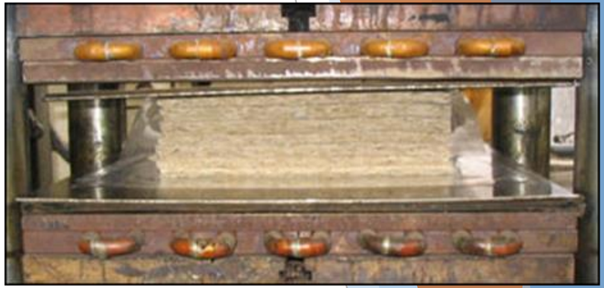
Two forms of materials were used:

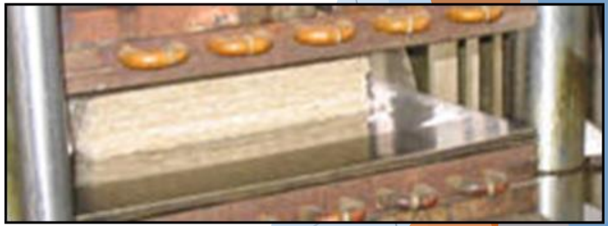
- **SMC (Sheet Molding Compounds)**
- **Pellets/granules**

SMC	Pellets
• Appropriate for big size panels • No molding tool is required • Multiple panels can be produced in one molding cycle • Cheaper manufacturing process • Better mechanical properties since longer fibers can be applied • Inappropriate for 3D moldings with complicated shape	• Inappropriate for big size panels • Molding tool is required • One panel only per cycle • Expensive manufacturing process • Only very short fibers can be used making panels with limited mechanical properties • Better control of fiber/resin ratio • Appropriate for 3D shapes with complicated shapes

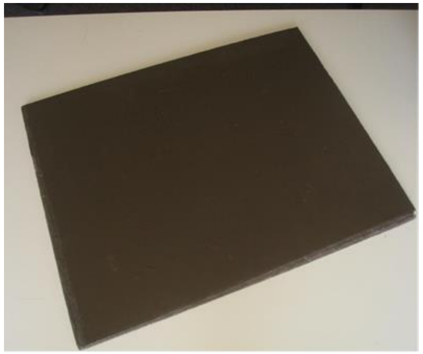
Applied processing techniques

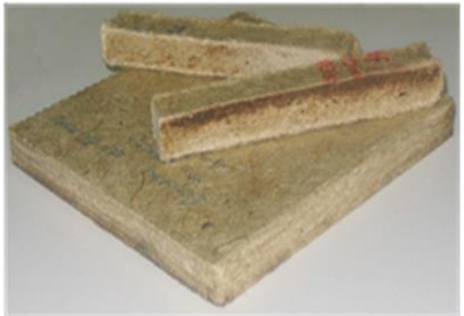
Open mold compression molding - Applicable for SMC



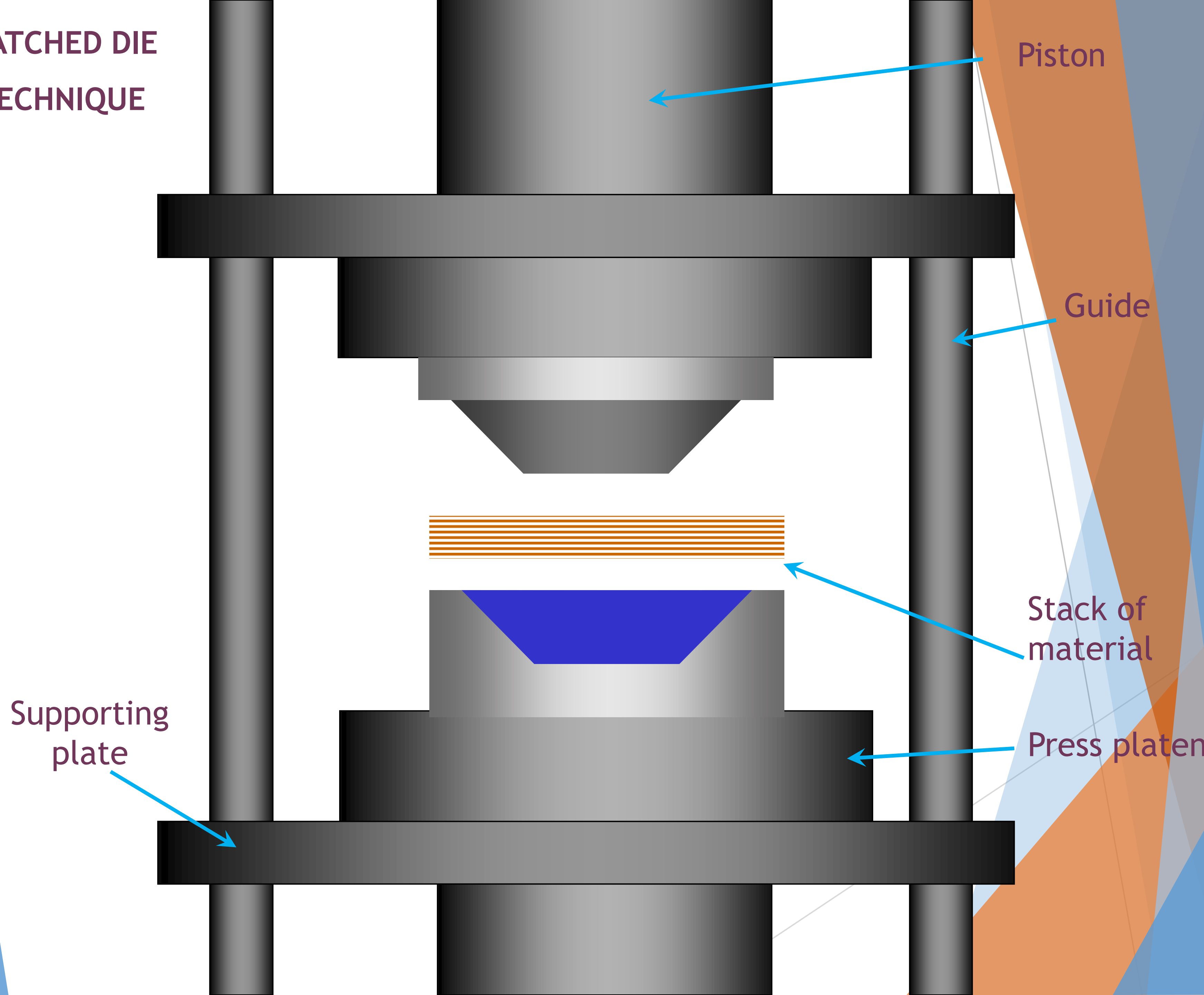
Composite plates based on kenaf fibers/thermoplastic polymers



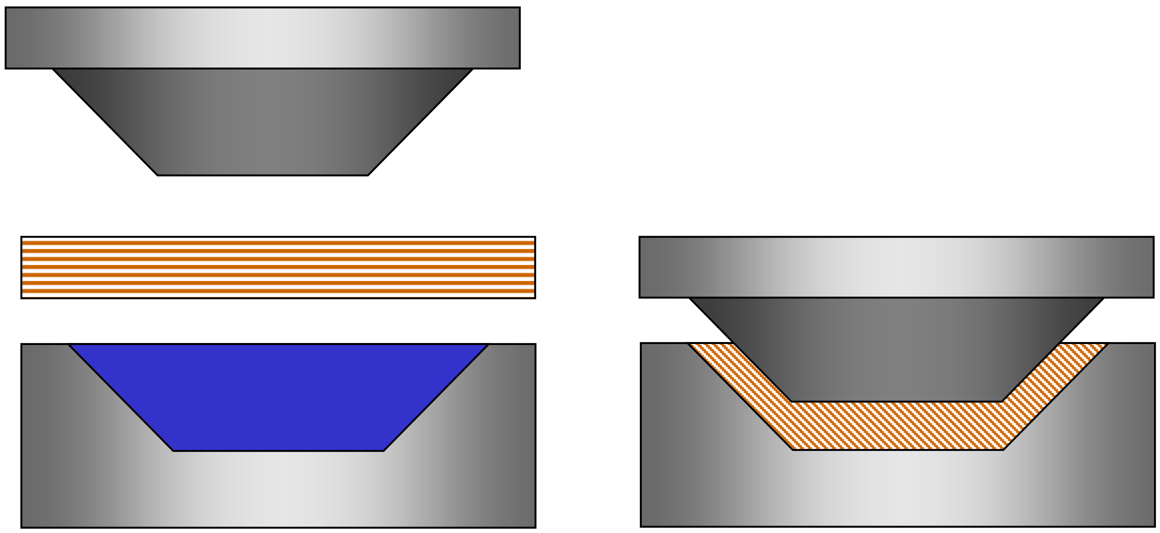


Property	Test Method	Composite based on kenaf fiber
Specific weight, g/cm ^{3}	JUS G.S2.51	0,93
Water absorption, %	ISO/DP 9674	30,5
Fire resistance	UL 94	burns
Flexural strength, MPa	DIN 53457	30,1
Flexural modulus, GPa	DIN 53457	9,0
Impact strength, kJ/m ^{2}	DIN 53453	65,5
Compression strength, MPa	DIN 53454	17,4

MATCHED DIE TECHNIQUE



Matched die molding

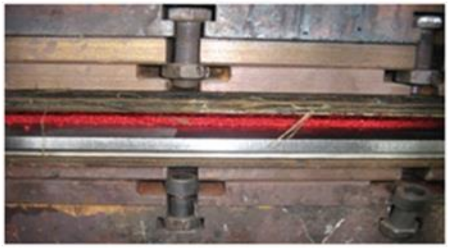


Open mold

Closed mold

Appropriate for BMC , pellets and for SMC (simple shapes only)

Matched die molding



pellets, granules
– rice hulls / PP
– rice hulls / PLA

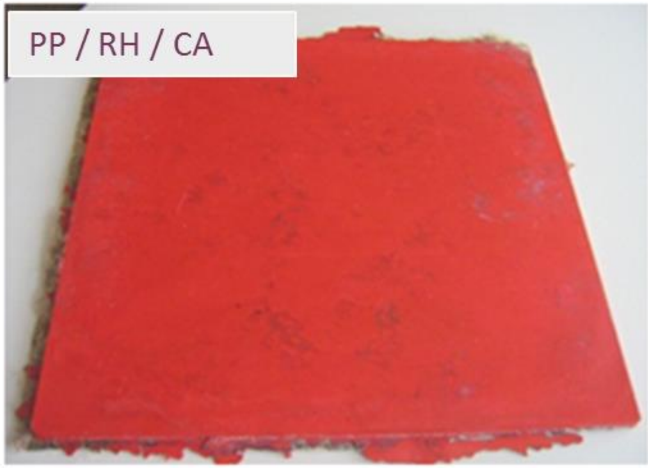
In both techniques main process parameters are:

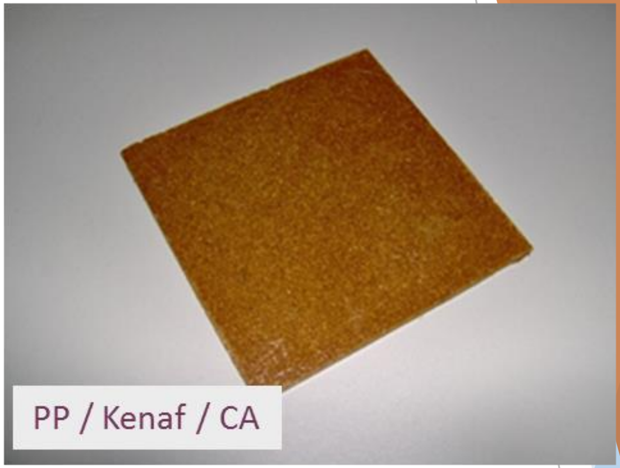
- **Temperature** – high enough to let the polymer melt

- **Time** - long enough to let the polymer flow

- **Holding pressure** – high enough to make the composite stiff, compact, void free

Composite plates based on kenaf fibers/thermoplastic polymers and rice hulls/thermoplastic polymers





The flexural tests

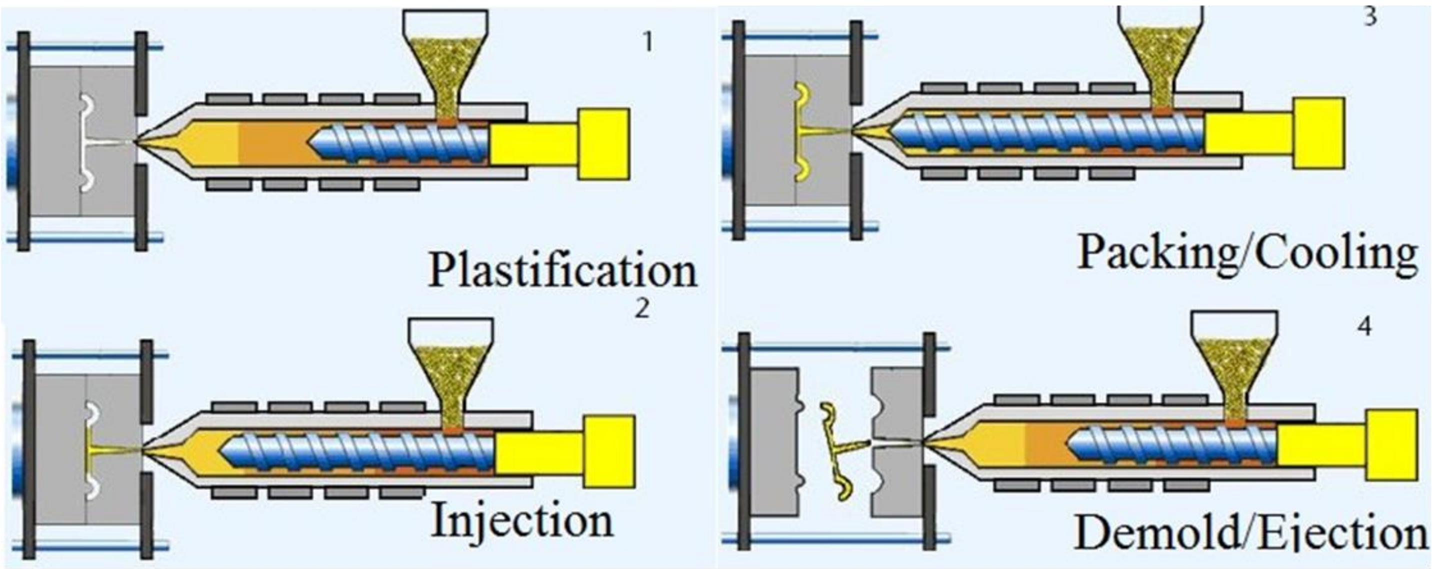
	Stress at peak, MPa	Modulus, MPa
PP / RH / CA 60/30/10 $^{wt}/_{wt}$	42,6	1941
PP / Kenaf / CA 60/30/10 $^{wt}/_{wt}$	51,3	2106
PLA / RH / CA 65/30/5 $^{wt}/_{wt}$	28,8	3031

The physical and mechanical properties of the composites produced by compression molding

Characteristics	Unit	Composite: **PP/K/CA**	Composite: **PP/RH/CA**	Composite: **PLA/K/CA**	Composite: **PLA/RH/CA**
Flexural strength	MPa	51.3 ± 4.84	42.6 ± 3.45	46.7± 3.83	28.8 ± 3.14
Flexural modulus	GPa	2.11 ± 0.07	1.94 ± 0.08	2.05 ± 0.11	1,63 ± 0.09
Impact strength	kJ/m^2	71.4 ± 4.67	69,2 ± 3.83	54.3 ± 3.49	48,7 ± 4.16
Compression strength	MPa	47.2 ± 2.93	36.3 ± 2.39	34,5 ± 3.11	21,6 ± 2.67
Compression modulus	GPa	1.86 ± 0.12	1,58 ± 0.09	1,74 ± 0.11	1,46 ± 0.07
Tensile strength	MPa	29.6 ± 3.84	22.7 ± 4.82	28.3 ± 6,54	26.7 ± 1,49
Tensile modulus	GPa	1.65 ±0,025	1.78 ± 0,014	2.87 ± 0.23	2.76± 0.11

Injection molding technique

Processing method for the manufacture of reinforced thermoplastic polymers



Processing cycle of conventional injection molding process

- *thermosetting, thermoplastic, fiber reinforced thermoplastics*
- *in many ways*
- *the most widely used*
- *length of fibers is short (about 0.2–0.4 mm)*
- *manufacturing a variety of parts*

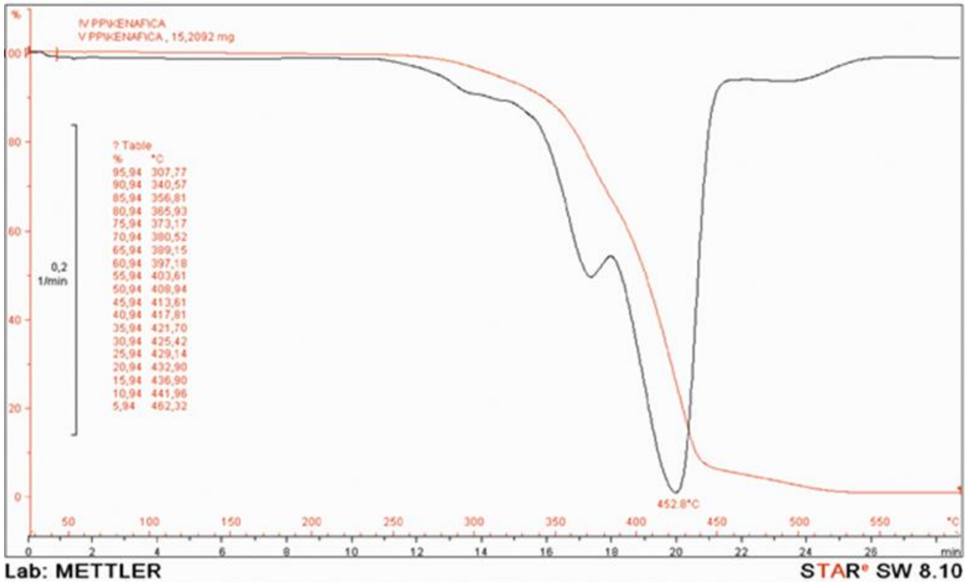
The mechanical properties of the injection molded composite samples

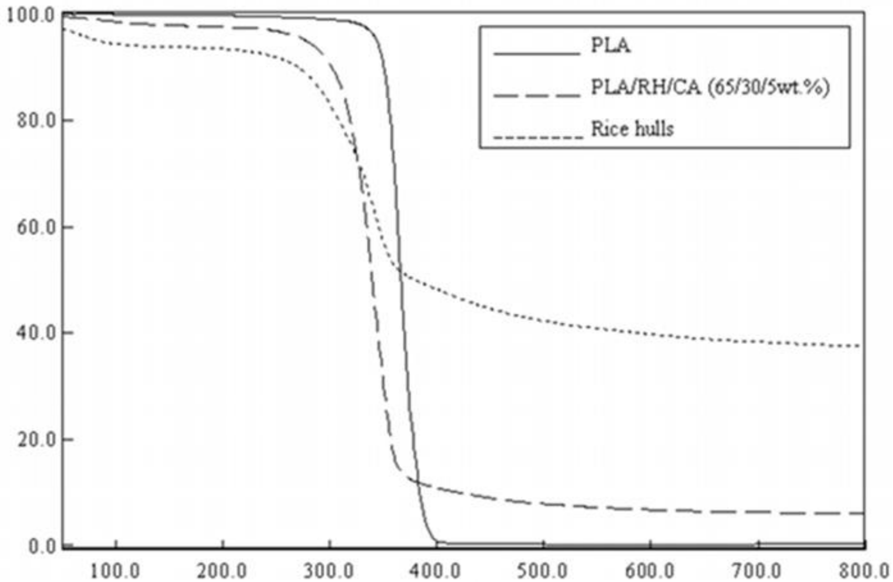
Characteristics	Unit	Composite: **PP/K/CA**	Composite: **PP/RH/CA**	Composite: **PLA/K/CA**	Composite: **PLA/RH/CA**
Flexural strength	MPa	40.1 ± 4.82	32.8 ± 3.44	34.1± 3.75	20,7 ± 2.82
Impact strength normal to the axis	kJ/m^2	57.1 ± 4.76	55.0 ± 4.13	40.7 ± 3.86	36.1 ± 3.46
Compression strength parallel to the axis	MPa	38.2 ± 2.93	28.1±2.43	26.5 ± 2.51	15.8 ± 1.91
Compression strength normal to the axis	GPa	27.8 ± 2.27	23.5 ± 2.44	22.6 ± 2.01	13.6 ± 1.83
Tensile strength	MPa	23.6 ± 2.14	17.9 ± 1.24	21.8 ± 1.02	20.6 ± 0.91

Injection molded inlet tube for “Tomos” water pump based on Kenaf/PLA

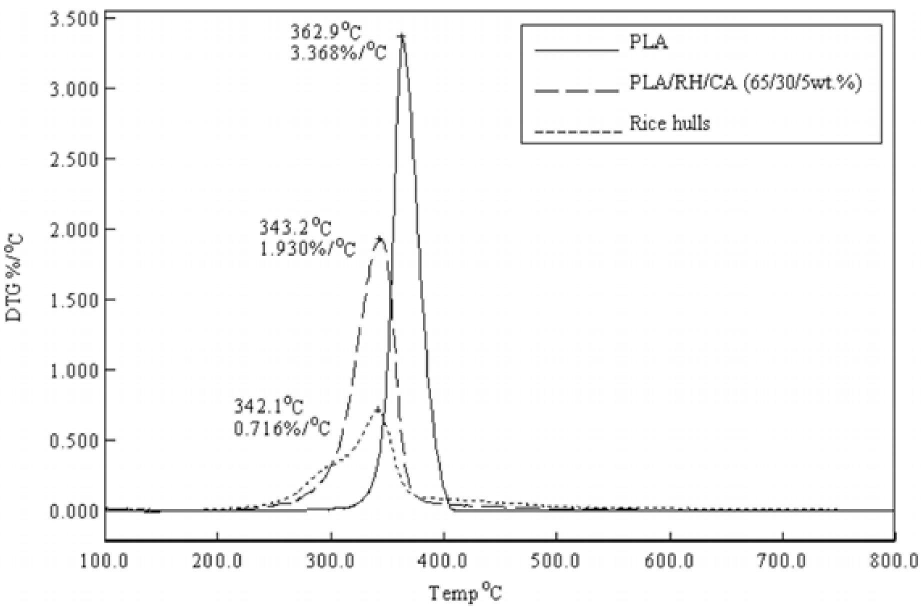
Thermogravimetric analyses (TGA)

Thermogravimetric curves, weight loss (TG) versus temperature





Derivative thermogravimetric curves, derivative weight loss (DTG) versus temperature



APPLICATION

- *as **non bearing material***
- *as interior partition walls, ceilings, flooring*
- *as thermal and acoustic insulation for improvement of energy efficiency in eco-buildings*
- *furniture*
- *automobile door panels, dashboards*
- *etc.*

Thank you