



Stabilitätspakt für Südosteuropa  
Gefördert durch Deutschland  
Stability Pact for South Eastern Europe  
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*Module Polymers – Ohrid, September 2014*

# Preparation and recycling of polymer eco-composites

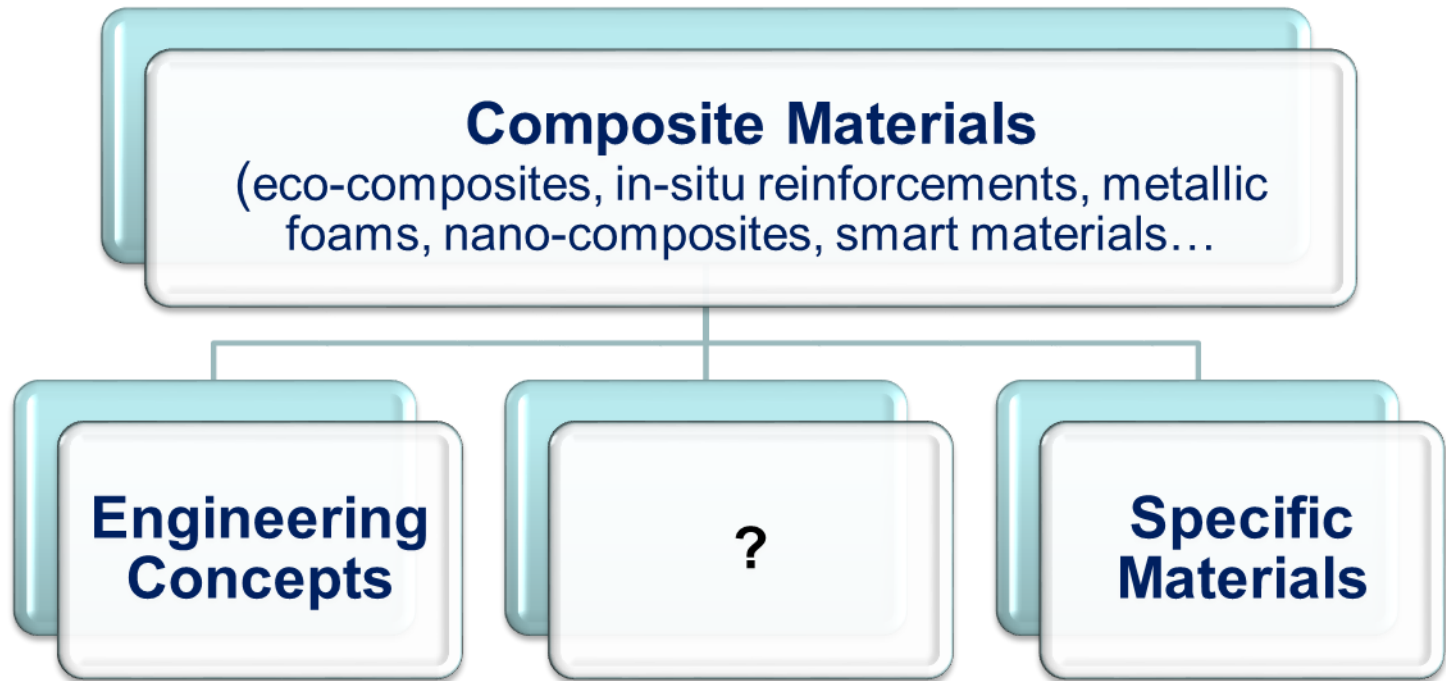
Dr. Vineta Srebrenkoska, associate professor  
Faculty of Technology,  
University Goce Delcev Shtip,  
Macedonia



# 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

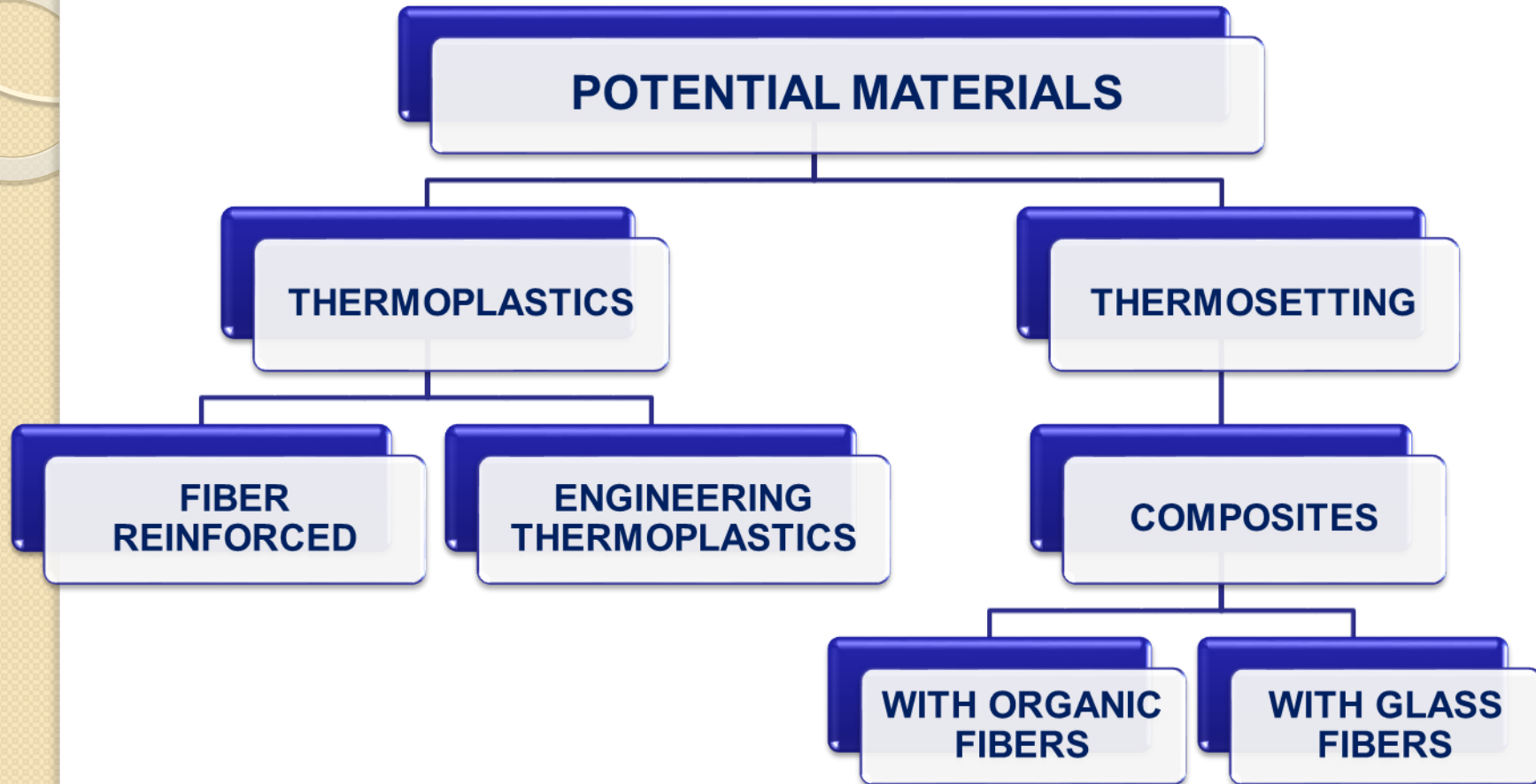
## ***Thermoplastic polymers:***

- ✓ *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.*

# 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*

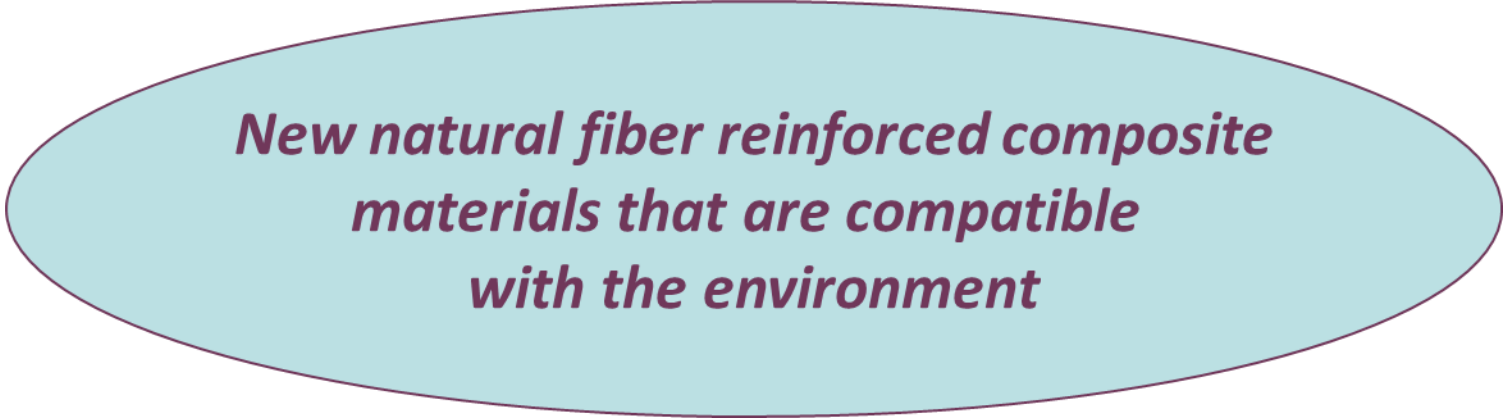




# DRIVING FORCE FOR A NEW GENERATION

## ***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

Application :

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

for example: *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

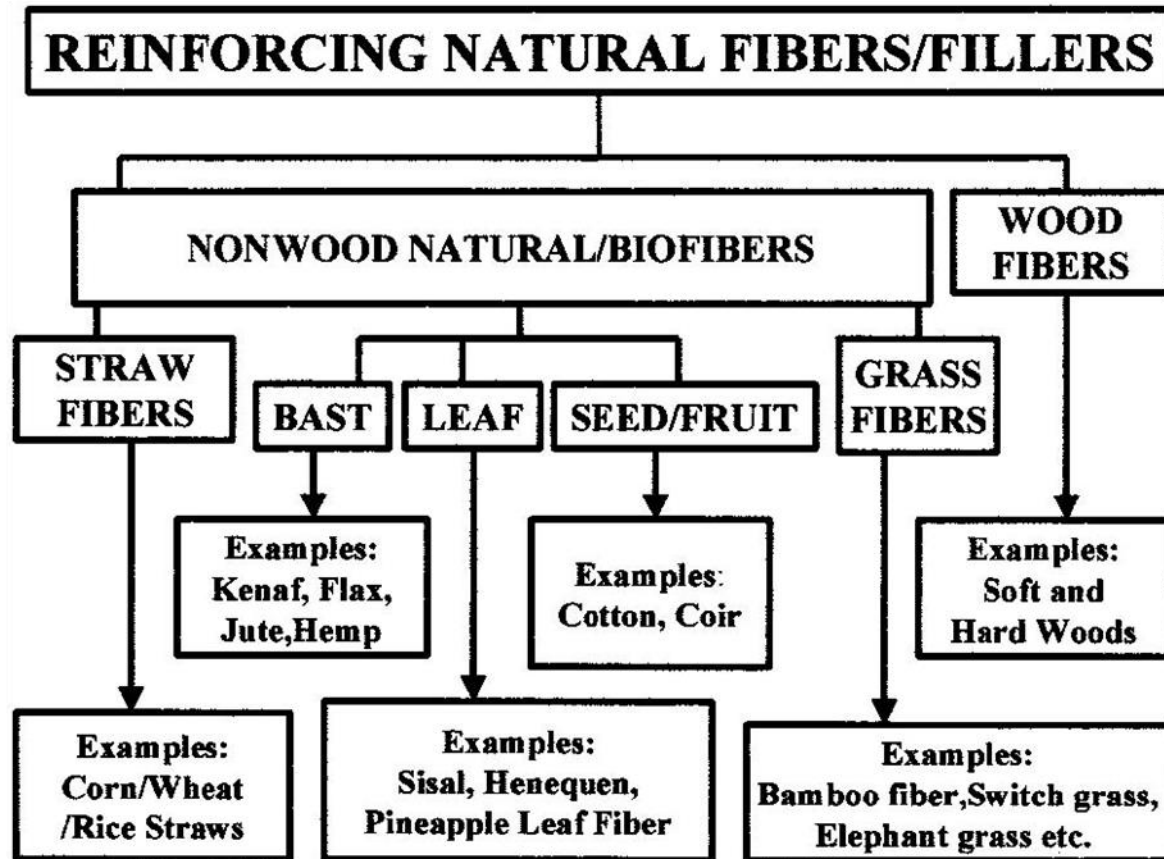
- growing interest in NF reinforced composites
- **high performance** in terms of mechanical properties, significant processing advantages, chemical resistance, and low cost/low density ratio.
- **environmental reasons** - increased interest in replacing reinforcement materials (inorganic fillers and 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
Polyethyleneterephthalate (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: $E_f=138$ GPa

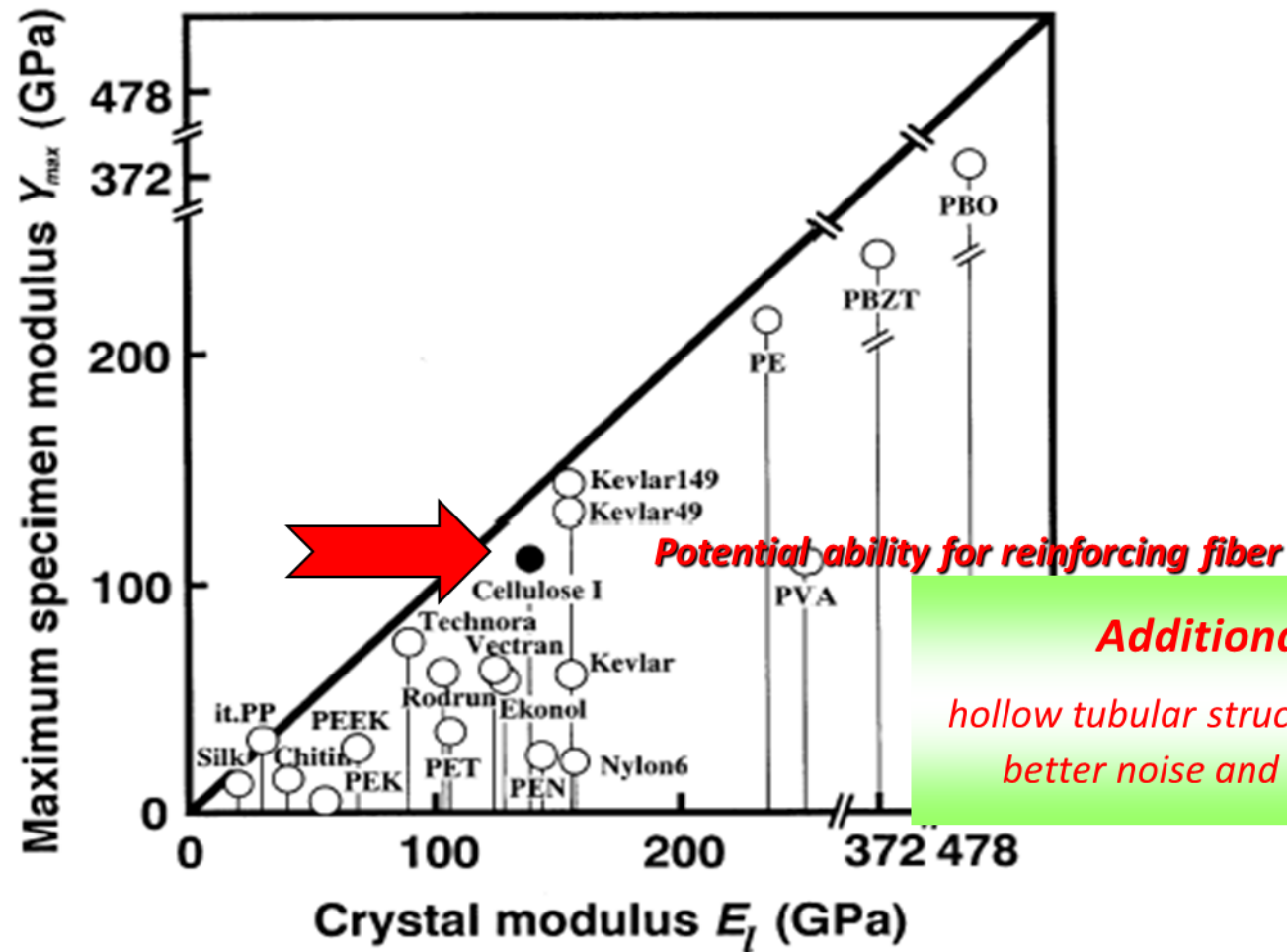


Fig. 2. Relationship between the crystal modulus  $E_f$  and the maximum specimen modulus  $Y_{max}$  already reported for various polymers.



## Basic properties of some natural fibers

Fiber	Density (g/cm <sup>3</sup> )	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/cm <sup>3</sup> )	Tensile strength (GPa)	Tensile modulus (GPa)	Specific strength (GPa/g cm <sup>3</sup> )	Specific modulus (GPa/g cm <sup>3</sup> )
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<sub>2</sub> 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:


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## 1. SMC

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

## 2. Pellets

- Kenaf/PLA
- Rice straw/PLA

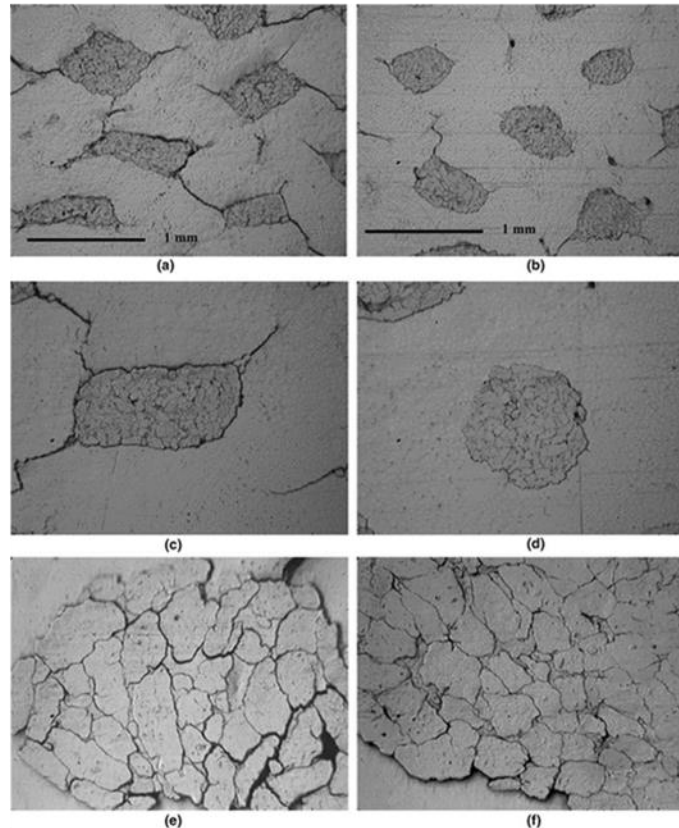


Different ratio of the main components + coupling agent

# INTERFACIAL ADHESION: natural fibers embedded in polymer matrix

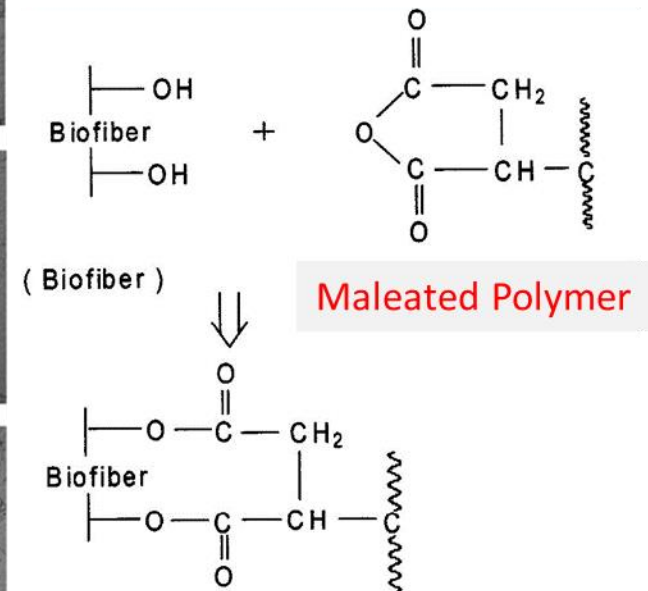
*Fiber/matrix interface region-  
key factor determining the load transfer*

- 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



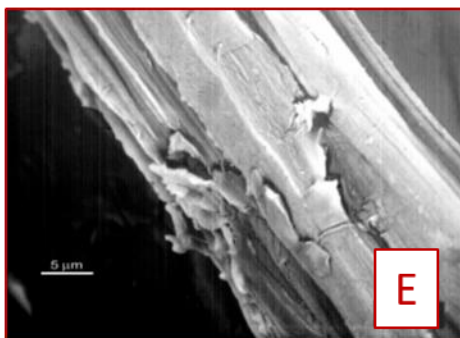
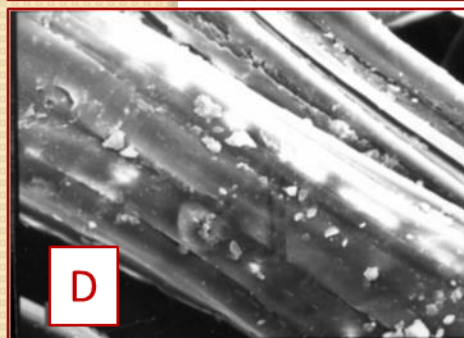
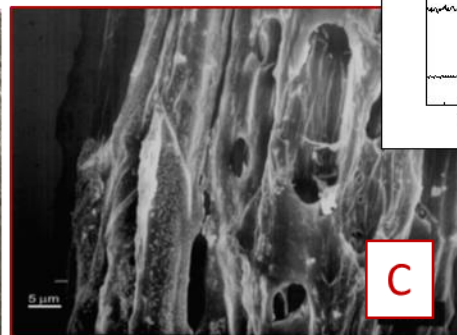
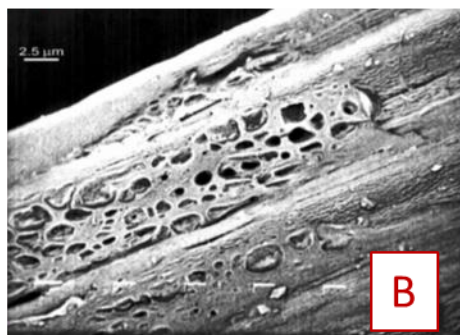
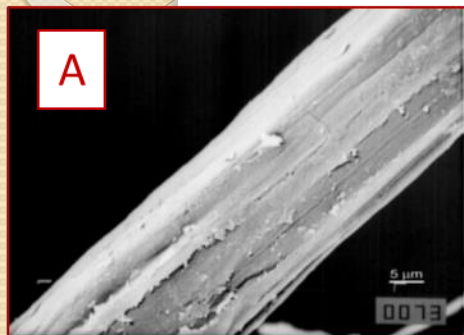
**Polymer matrix modification:  
creation of chemical bonds**



# FP6 Project ECO-PCCM:

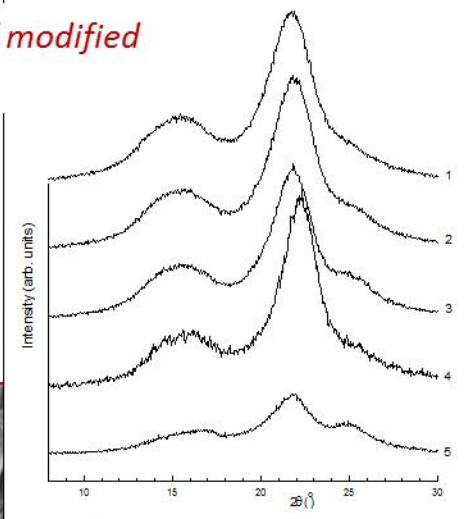
WAXS analysis, FTIR, SEM  
of modified **kenaf** fibers

*SEM images of kenaf samples*

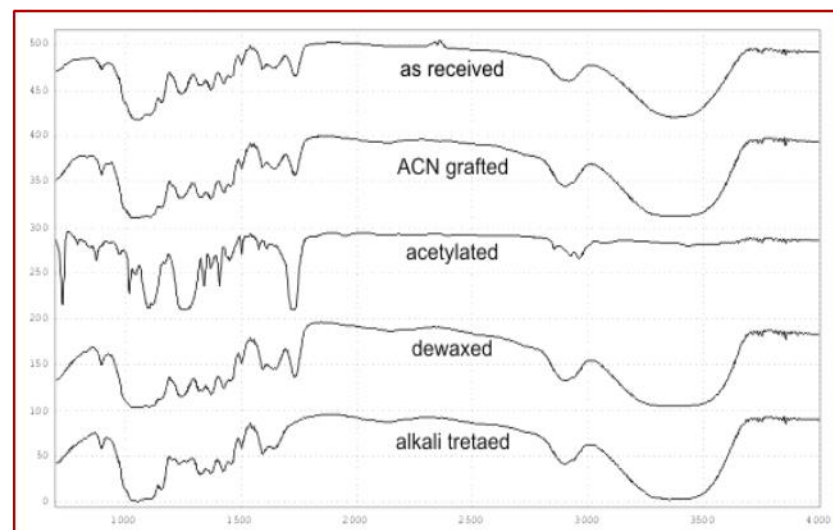


*A – As received fiber  
B – ACN grafted fiber  
C – Acetylated fiber  
D – Dewaxed fiber  
E – Alkali treated fiber*

*WAXS patterns of modified kenaf fibers*



*FTIR spectra of treated kenaf fibres*



## Codes of composite samples

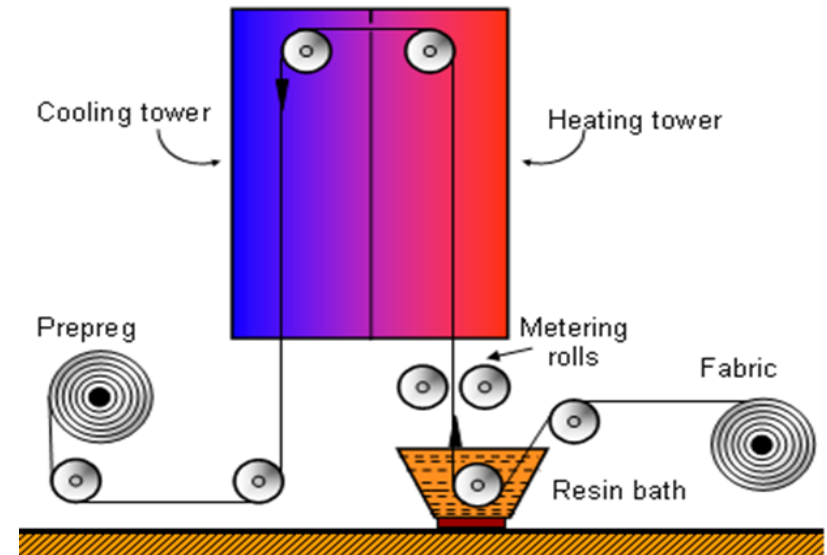
Codes	Matrix (wt%)		Fiber/Filler		Coupling agent (CA)	
	Type	Content (wt%)	Type	Content (wt%)	Type	Content (wt%)
PP/K/CA	PP	65	Kenaf fibers	30	MAPP	5
PP/RH/CA			Rice Hulls			
PLA/K/CA			Kenaf fibers			
PLA/RH/CA			Rice Hulls			

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 preregs 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



# 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





## FP6 Project ECO-PCCM:

Two forms of materials were used:

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



SMC	Pellets
<ul style="list-style-type: none"><li>• Appropriate for big size panels</li><li>• No molding tool is required</li><li>• Multiple panels can be produced in one molding cycle</li><li>• Cheaper manufacturing process</li><li>• Better mechanical properties since longer fibers can be applied</li><li>• Inappropriate for 3D moldings with complicated shape</li></ul>	<ul style="list-style-type: none"><li>• Inappropriate for big size panels</li><li>• Molding tool is required</li><li>• One panel only per cycle</li><li>• Expensive manufacturing process</li><li>• Only very short fibers can be used making panels with limited mechanical properties</li><li>• Better control of fiber/resin ratio</li><li>• Appropriate for 3D shapes with complicated shapes</li></ul>

**SMC**

Piston

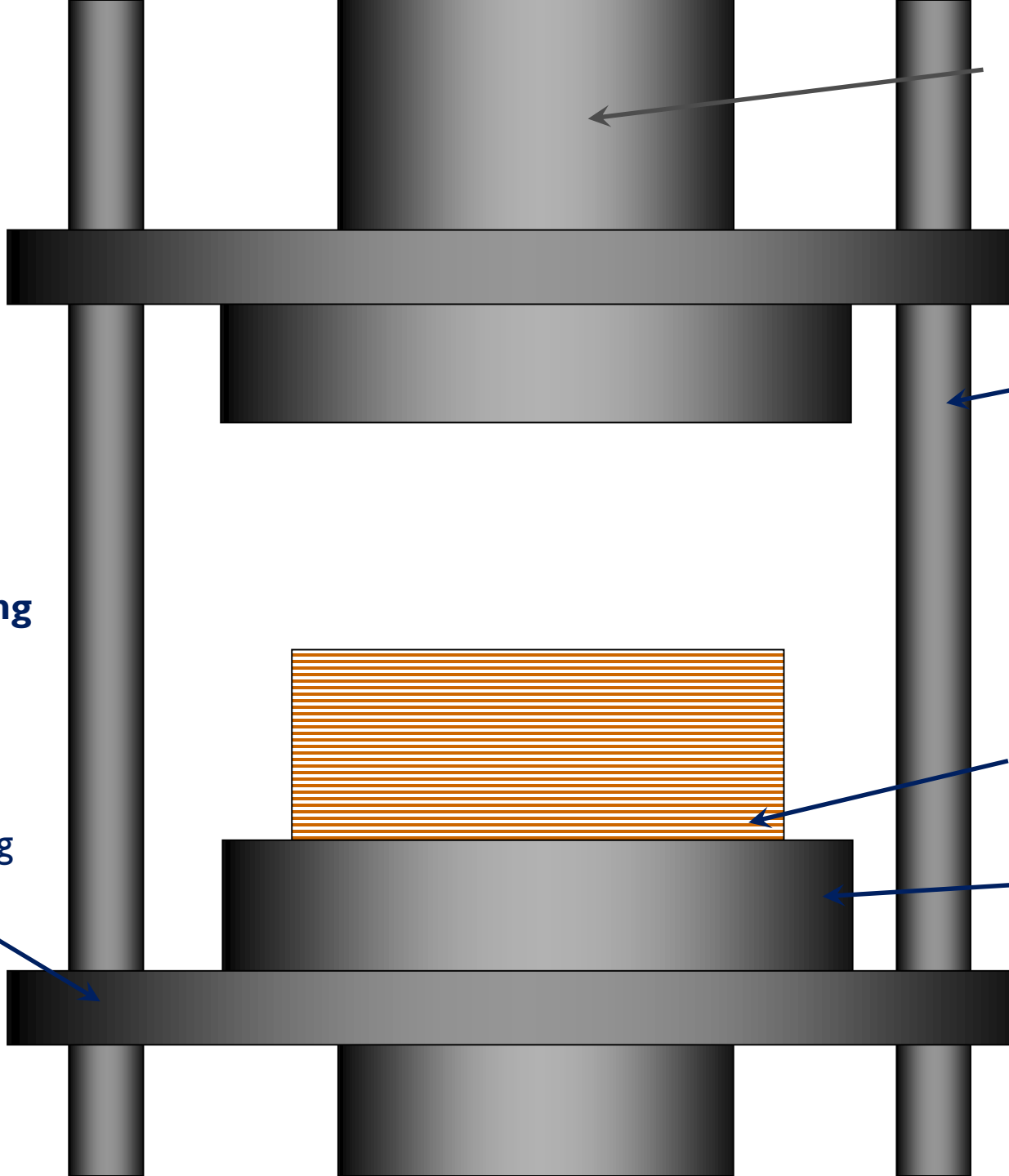
Guide

**No mold,  
single-opening  
press**

Stack of  
material  
(SMC layers)

Heated press  
platen

Supporting  
plate



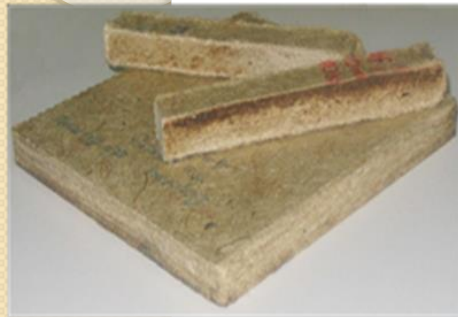
# Applied processing techniques

Open mold compression molding - Applicable for SMC



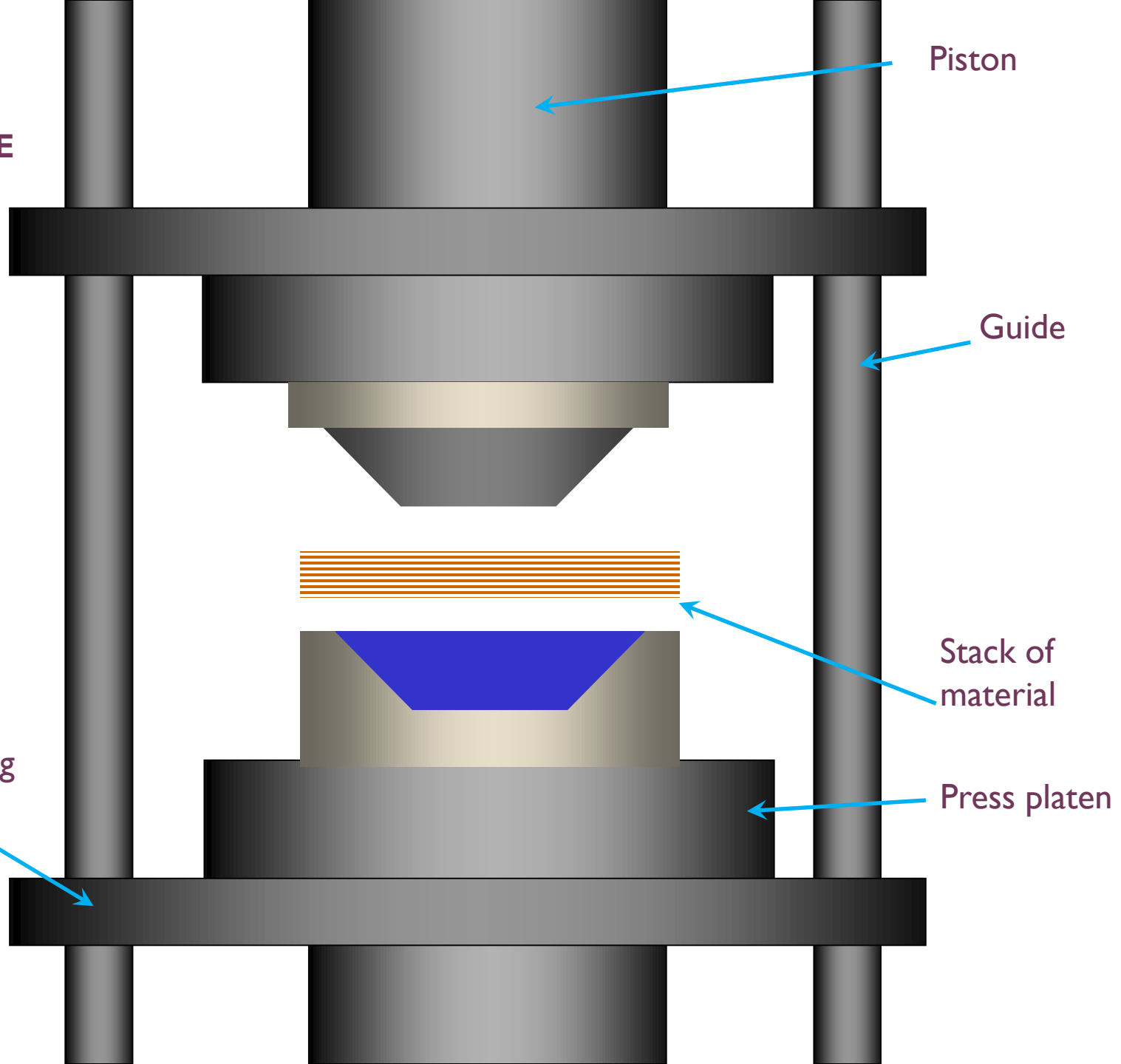


# Composite plates based on kenaf fibers/thermoplastic polymers

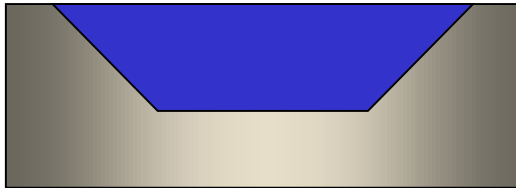


Property	Test Method	Composite based on kenaf fiber
Specific weight, g/cm <sup>3</sup>	JUS G.S2.51	0,93
Water absorption, %	ISO/DP 9674	30,5
Fire resistance	UL 94	burns
Flexural strength, MPa	DIN 53457	30,1
Flexural modulus, GPa	DIN 53457	9,0
Impact strength, kJ/m <sup>2</sup>	DIN 53453	65,5
Compression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

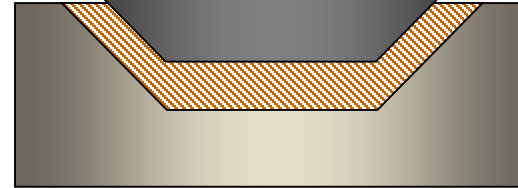
**MATCHED  
DIE  
TECHNIQUE**



# Matched die molding



Open mold



Closed mold

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

# Matched die molding



*pellets, granules*

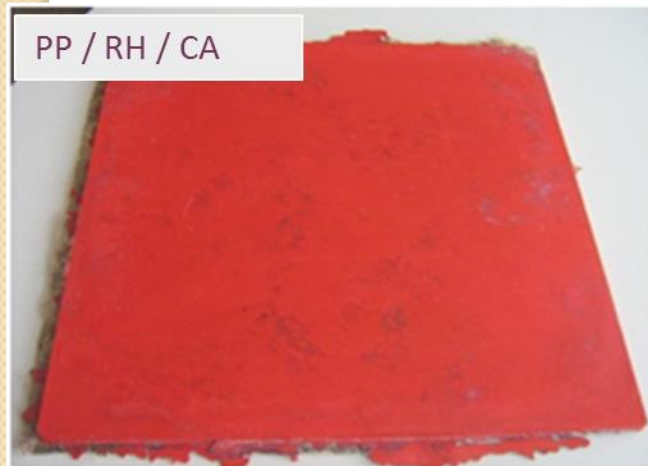
*– rice hulls / PP*

*– 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 <sup>wt</sup> / <sub>wt</sub>	42,6	1941
PP / Kenaf / CA 60/30/10 <sup>wt</sup> / <sub>wt</sub>	51,3	2106
PLA / RH / CA 65/30/5 <sup>wt</sup> / <sub>wt</sub>	28,8	3031

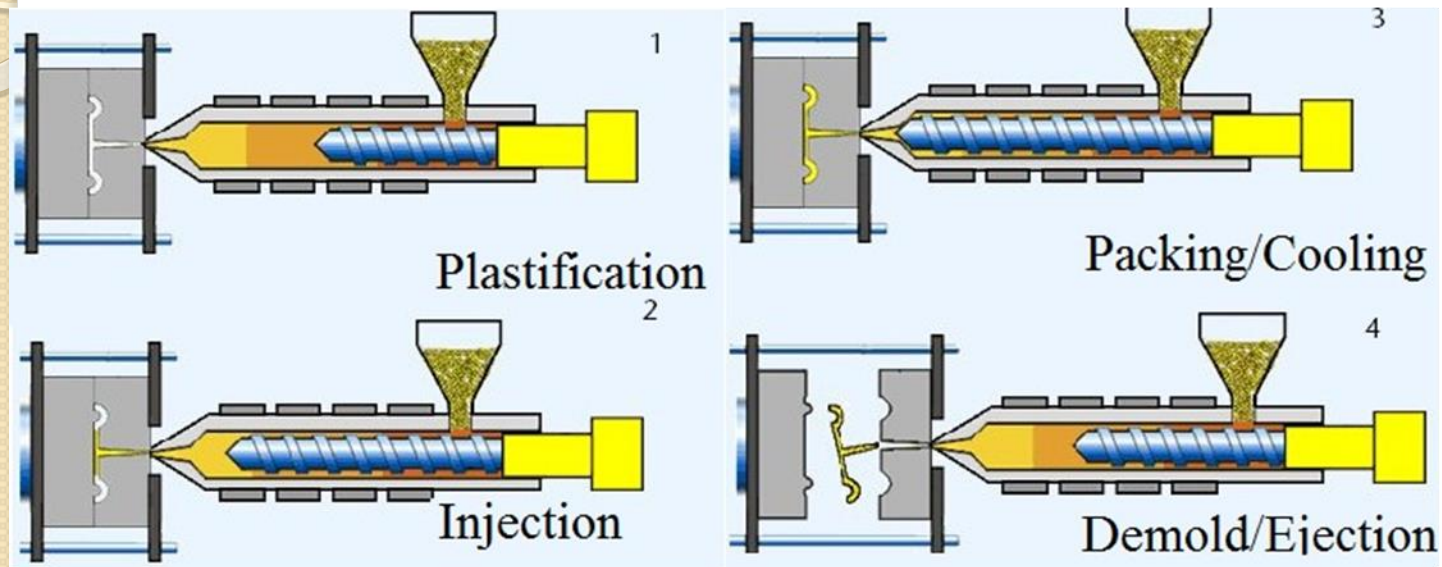
The physical and mechanical properties of the composites produced by compression molding

Characteristics	Unit	Composite: <b>PP/K/CA</b>	Composite: <b>PP/RH/CA</b>	Composite: <b>PLA/K/CA</b>	Composite: <b>PLA/RH/CA</b>
Flexural strength	MPa	$51.3 \pm 4.84$	$42.6 \pm 3.45$	$46.7 \pm 3.83$	$28.8 \pm 3.14$
Flexural modulus	GPa	$2.11 \pm 0.07$	$1.94 \pm 0.08$	$2.05 \pm 0.11$	$1.63 \pm 0.09$
Impact strength	$\text{kJ/m}^2$	$71.4 \pm 4.67$	$69.2 \pm 3.83$	$54.3 \pm 3.49$	$48.7 \pm 4.16$
Compression strength	MPa	$47.2 \pm 2.93$	$36.3 \pm 2.39$	$34.5 \pm 3.11$	$21.6 \pm 2.67$
Compression modulus	GPa	$1.86 \pm 0.12$	$1.58 \pm 0.09$	$1.74 \pm 0.11$	$1.46 \pm 0.07$
Tensile strength	MPa	$29.6 \pm 3.84$	$22.7 \pm 4.82$	$28.3 \pm 6.54$	$26.7 \pm 1.49$
Tensile modulus	GPa	$1.65 \pm 0.025$	$1.78 \pm 0.014$	$2.87 \pm 0.23$	$2.76 \pm 0.11$



# 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: <b>PP/K/CA</b>	Composite: <b>PP/RH/CA</b>	Composite: <b>PLA/K/CA</b>	Composite: <b>PLA/RH/CA</b>
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 <sup>2</sup>	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*

# Investigation of the recycling ability of eco-composites

**PP matrix** - extruded one and two times (PP x1 and PP x2)

**PLA matrix** - extruded one time (PLA x1) into strips

**PP recycled based composites**

**PLA recycled based composites**

**Eco-composites - by recycling one and two times**

- it has been molded by thermo compression
- plates with thickness 3 mm are produced



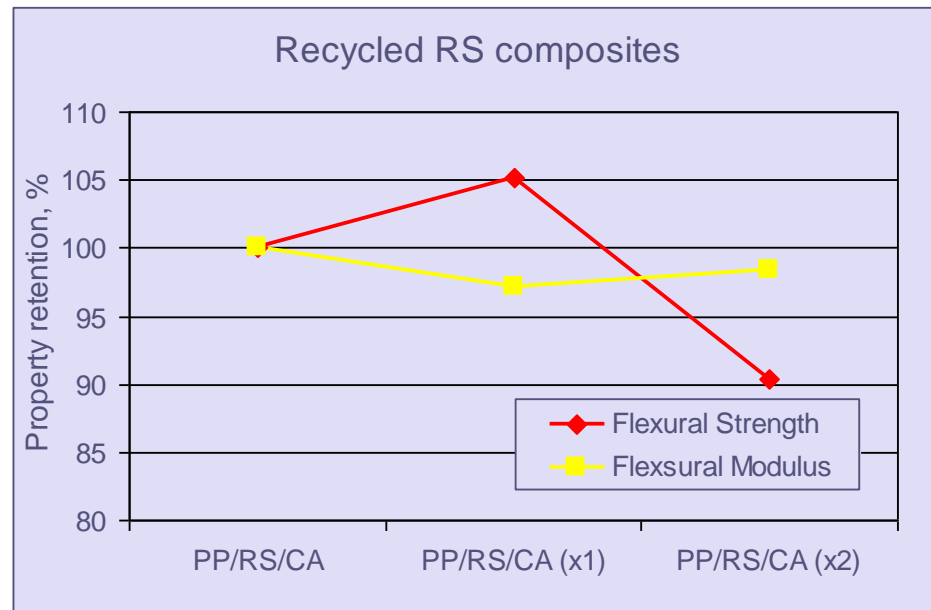
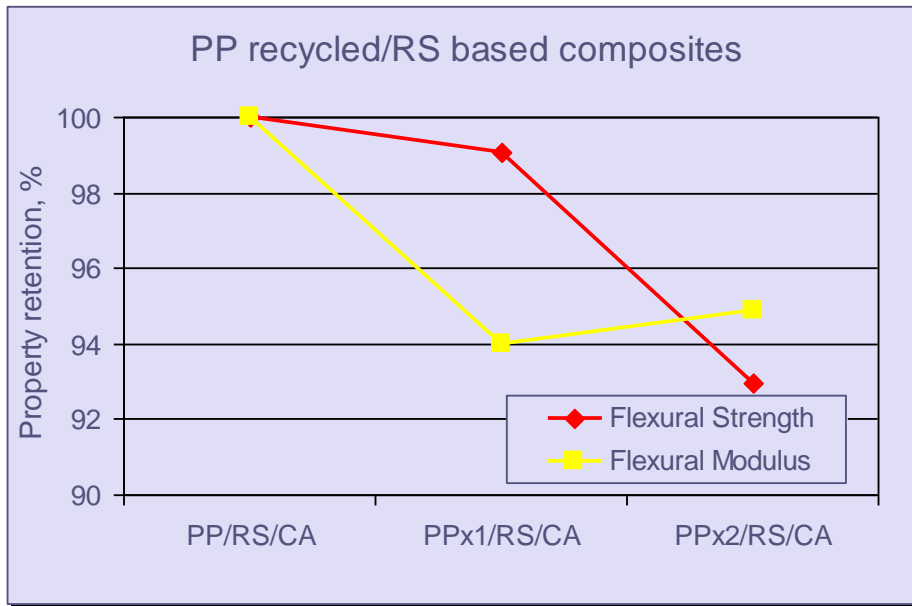
## The flexural tests for PP recycled based composites

	Stress at peak, MPa	Standard Deviation	Modulus, MPa	Standard Deviation
PP / RS / CA 60/30/10 <sup>wt/wt</sup>	42,6	3,4	1941	82
PPx1 / RS / CA 60/30/10 <sup>wt/wt</sup>	42,2	1,2	1825	41
PPx2 / RS / CA 60/30/10 <sup>wt/wt</sup>	39,6	4,6	1842	63
PP / Kenaf / CA 60/30/10 <sup>wt/wt</sup>	51,3	4,8	2106	68
PPx1 / Kenaf / CA 60/30/10 <sup>wt/wt</sup>	51,1	3,0	2346	204

## The flexural tests for PLA recycled based composites

	Stress at peak, MPa	Standard Deviation	Modulus, MPa	Standard Deviation
PLA / RS / CA 65/30/5 <sup>wt/wt</sup>	28,8	6,6	3031	182
PLAx1 / RS / CA 65/30/5 <sup>wt/wt</sup>	14,8	1,3	2275	457

# Recycling properties



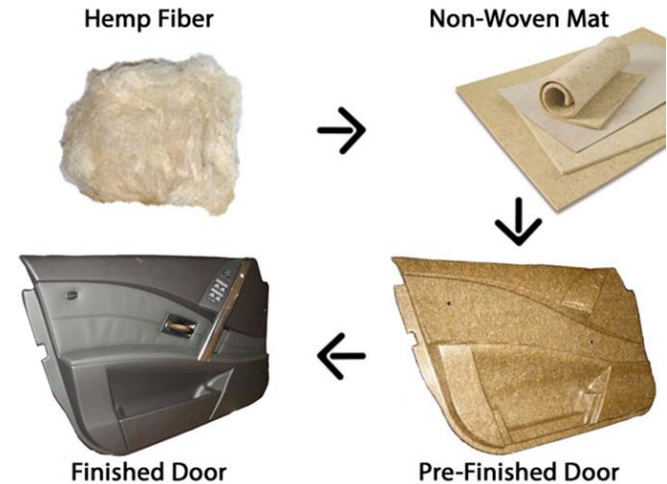
*Recycled polymer matrices could be used for production of new composites*

*Recycled eco-composites could be reused as composite components*

*Polymer eco-composites represent a good potential for utilization after recycling*

# 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**