RESEARCH & DEVELOPMENT OF GREEN COMPOSITES IN CHINA AND IN COOPERATION WITH EUROPE

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Organisation: BIAM, CHINA

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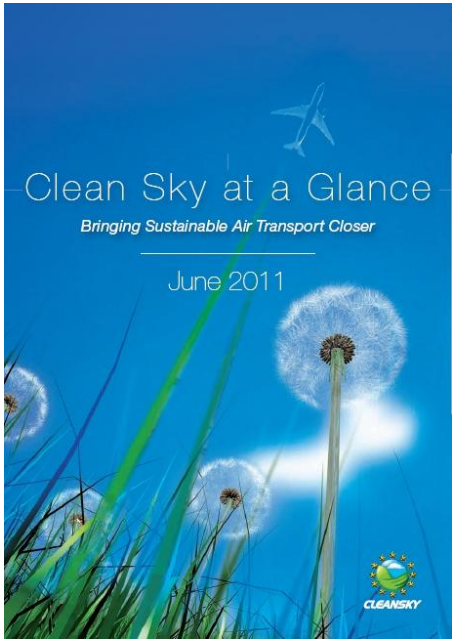
Outline

1. Why to jointly develop green composites for aviation?
2. Bio-sourced resins as matrices and plant fibers as reinforcing component for biocomposites
3. Special problem with biocomposites: flame retardation and hygrothermal stabilization
4. Trial application and demonstration
5. Conclusions and outlook

Green Trend for Aviation

The **CLEAN SKY** is to identify, develop and validate the key technologies necessary to achieve major steps towards the **ACARE** environmental goals for 2020 when compared to 2000 levels:

- Fuel consumption and carbon dioxide (CO_2) emissions reduced by 50%
- Nitrous oxides (NO_X) emissions reduced by 80%
- Perceived external noise reduction of 50%
- Improved environmental impact of the lifecycle of aircraft and related products.

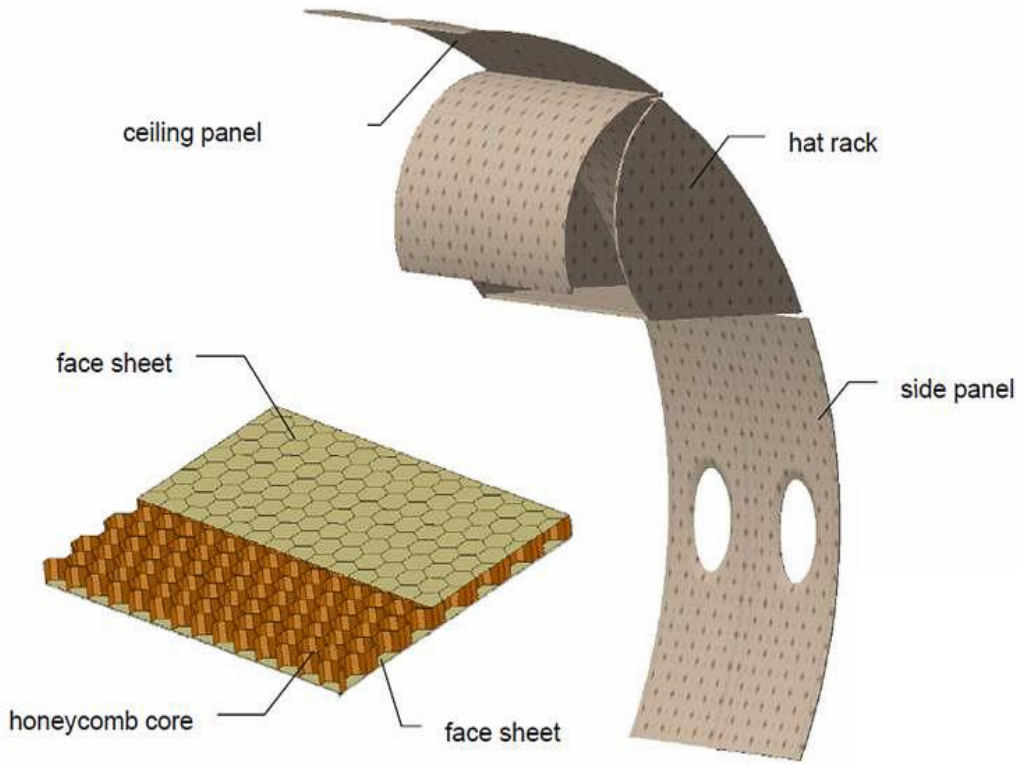


ECO-COMPASS

- **Ecological and Multifunctional Composites for Application in Aircraft Interior and Secondary Structures (ECO-COMPASS)**
- The overall objective in **ECO-COMPASS** is to develop and assess **multifunctional** and **ecological improved composites** for application in aircraft secondary structures and interior.
- Approved by the Chinese and European government, and it started in April 2016, with a duration of 3 years (2016-2018)

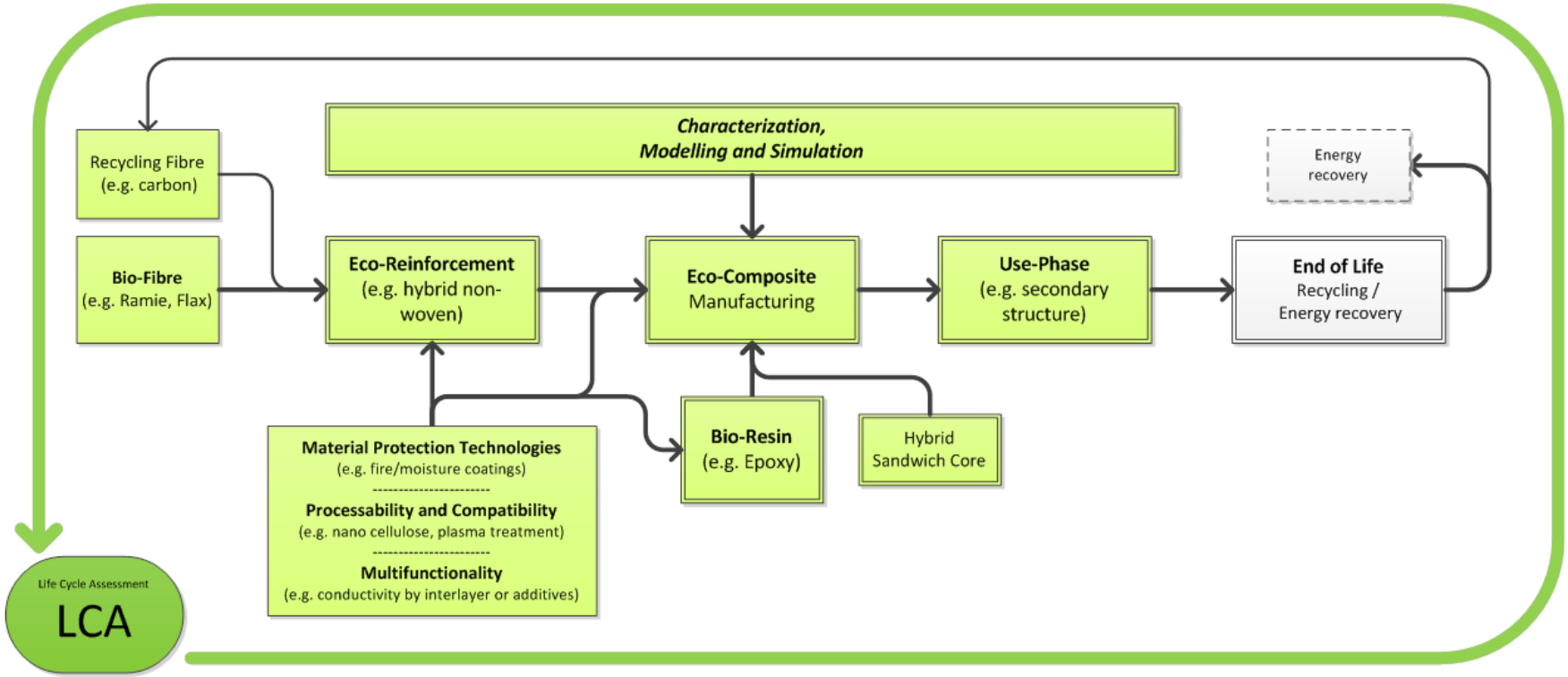
Potential Application: Interior

- Challenges
  - Fire properties
  - Weight
  - Sensitivity for liquids and humidity
- Possible use-cases
  - Sidewalls
  - Overhead Stowage Bins
  - Wall Partitions
  - Ceiling Panels
  - Galley



Potential Application: Secondary Structure

Life-Cycle-Assessment



Consortia

8 EUROPEAN PARTNERS
FROM 6 COUNTRIES

11 CHINESE PARTNERS

AIRBUS GROUP INNOVATIONS

CENTRE INTERNACIONAL DE METODES NUMERICS EN ENGINYERIA

DEUTSCHES ZENTRUM FUER LUFT - UND RAUMFAHRT EV

INSTITUTO DE CIENCIA E INOVACAO EM ENGENHARIA MECANICA E ENGENHARIA INDUSTRIAL

ACONDICIONAMIENTO TARRASENSE ASSOCIACION

L-UP

UNIVERSITY OF MANCHESTER

UNIVERSITY OF PATRAS

AVIC COMPOSITE CORPORATION, LTD

CHINA AVIATION INDUSTRY GENERAL AIRCRAFT CO.,LTD

AVIC BEJING INSTITUTE OF AERONAUTICAL MATERIALS

AVIC HARBIN AIRCRAFT INDUSTRY (GROUP) CO. LTD

HARBIN INSTITUTE OF TECHNOLOGY

AVIC HEFEI HANGTAI ELECTROPHYSICS CO.,LTD

NINGBO INSTITUTE OF INDUSTRIAL TECHNOLOGY,CHINESE ACADEMY OF SCIENCES.

SHANGHAI AIRCAFT MANUFACTURING CO.,LTD

SHANDONG UNIVERSITY

TONGJI UNIVERSITY

AVIC XI'AN AIRCRAFT INDUSTRY (GROUP) COMPANY LTD

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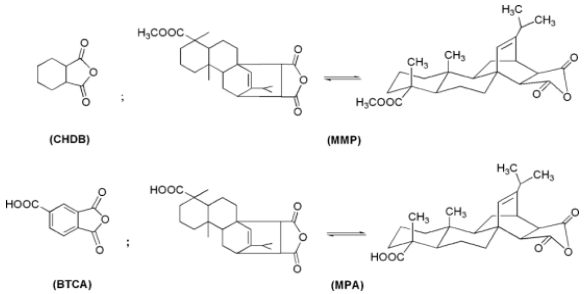
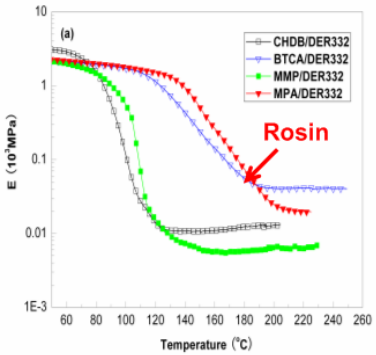
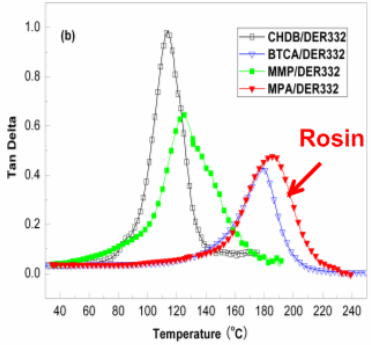
Bio-sourced Resins for Composites

- Two anhydride-type EP curing agents (maleopimaric acid /MPA and methyl maleopimarate /MMP) were synthesized from rosin acids.







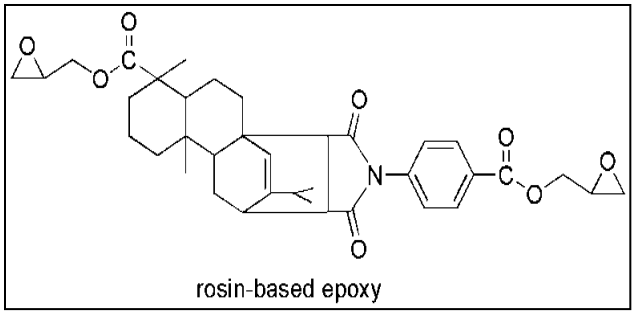
- For comparison, their commercial petroleum-based analogs (1,2-cyclohexanedicarboxylic anhydride /CHDB and 1,2,4-benzenetricarboxylic anhydride /BTCA) were also used to cure liquid EP resins DER332 (2,2-bis[4-(glycidyloxy)phenyl] propane, 171-175 g/eq).

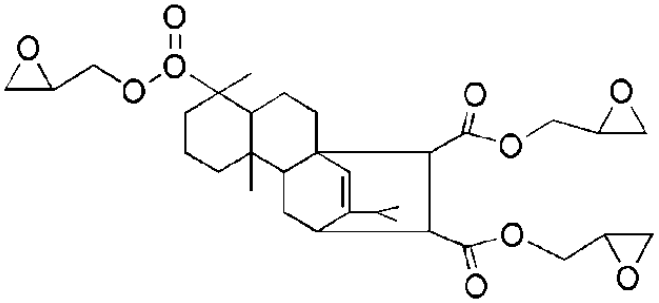
- MMP- and MPA-cured EP show similar modulus levels as systems cured by CHDB and BTCA, but yield higher Tg, being attributable to the fact that the bulky fused ring structures of MMP and MPA restrict segmental mobility levels between crosslink's, resulting in higher *T*g levels.

X. Liu, J. Zhang, High-performance biobased epoxy derived from rosin, Polym. Int. 59(2010) 607-609

Mechanical Properties of A Rosin-Epoxy

- Target and references

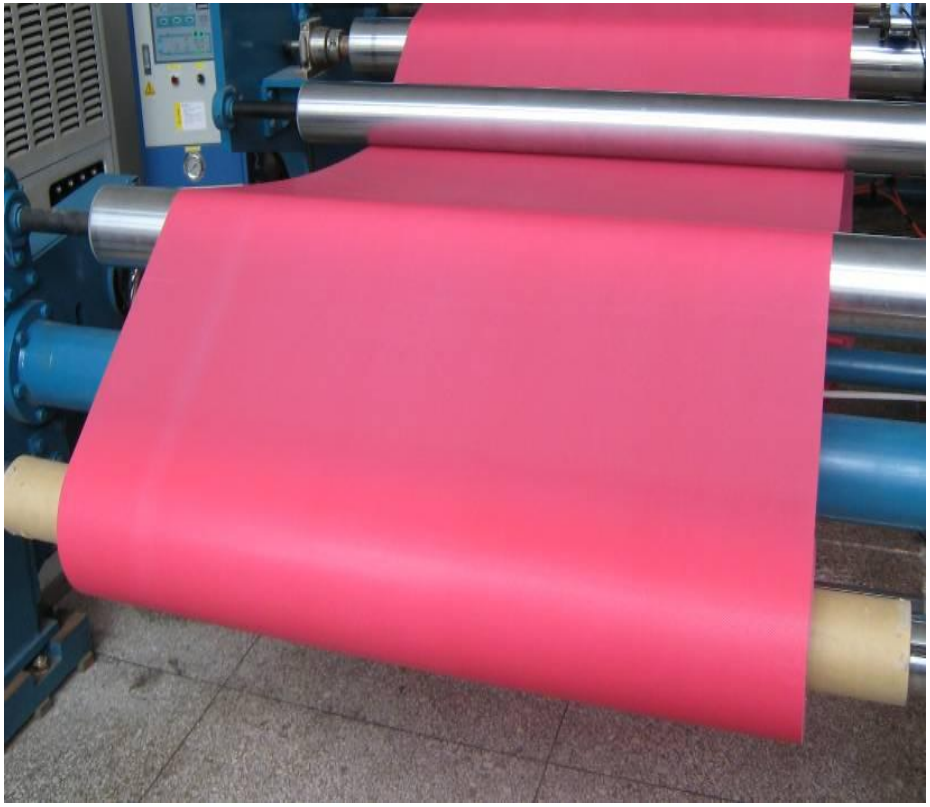


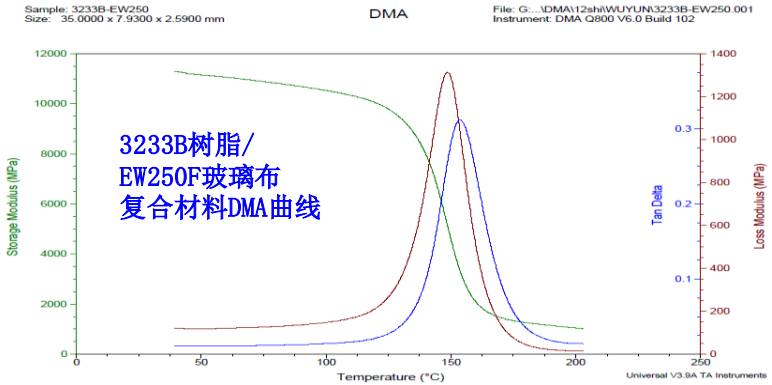


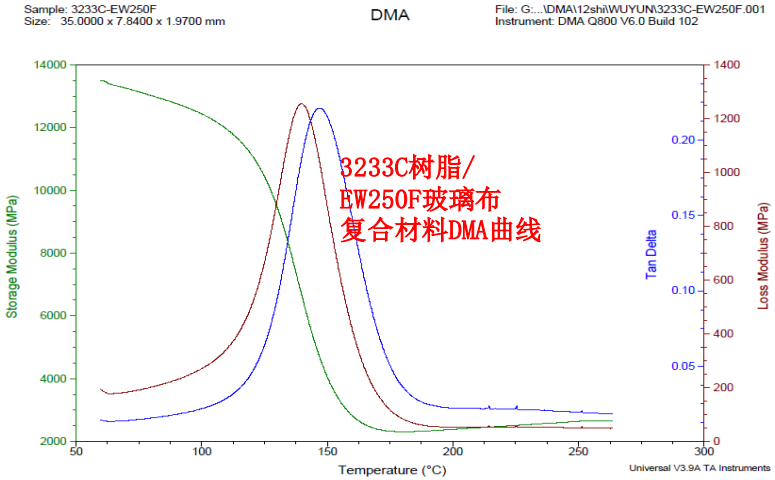
Items	Current Results	Target	Bisphenol A Epoxy
Tensile Stress	~70MPa	75-90MPa	60-90MPa
Tensile Modulus	2.8GPa	3.5GPa	2-3.5GPa
Tg（°C）	120-130℃	70-150°C	90-150°C
State（25°C）	liquid	liquid/solid	Liquid/solid

X. Liu, J. Zhang, High-performance biobased epoxy derived from rosin, Polym. Int. 59(2010) 607-609

Rosin-based EP Prepregs



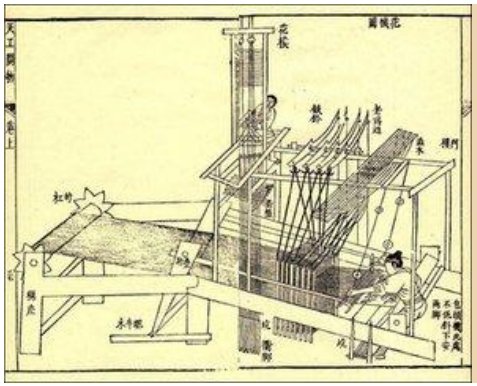




What Fibers Suitable As Reinforcement?

Fiber	Density (g/cm^3)	Elongation at break (%)	Tensile Strength (MPa)	Tensile Modulus (GPa)
Ramie	1.5	3.6-3.8	400-938	44-128
Sisal	1.45	2.0-2.5	511-700	3.0-98
Jute	1.3-1.45	1.5-1.8	270-900	10-30
Kenaf	/	2.7	427-519	23.1-27.1
Hemp	1.48	1.6	270-900	20-70
E-Glass	2.60	0.2-0.3	3500	72
Kevlar	1.44	2.3-4.0	3900	131

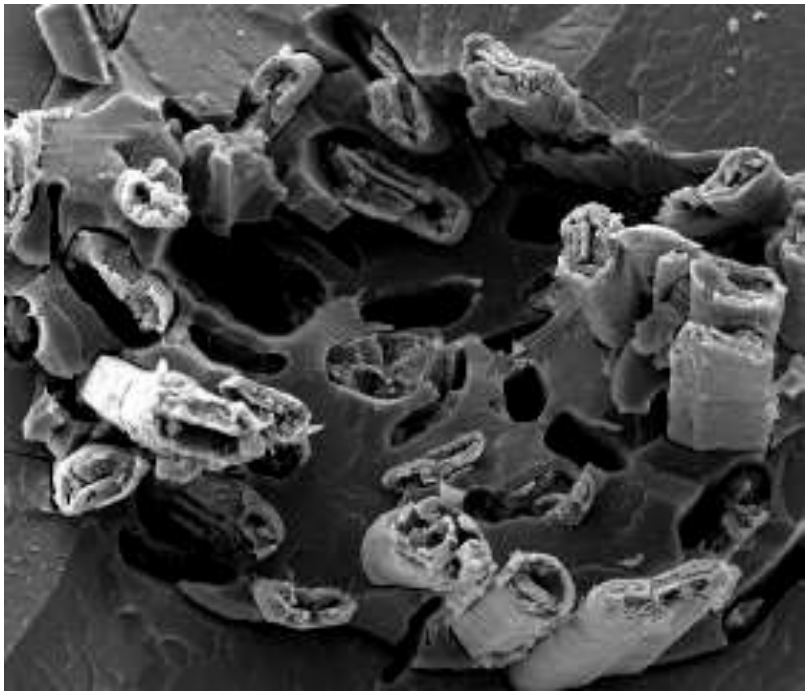
Ramie, China Grass (夏布)

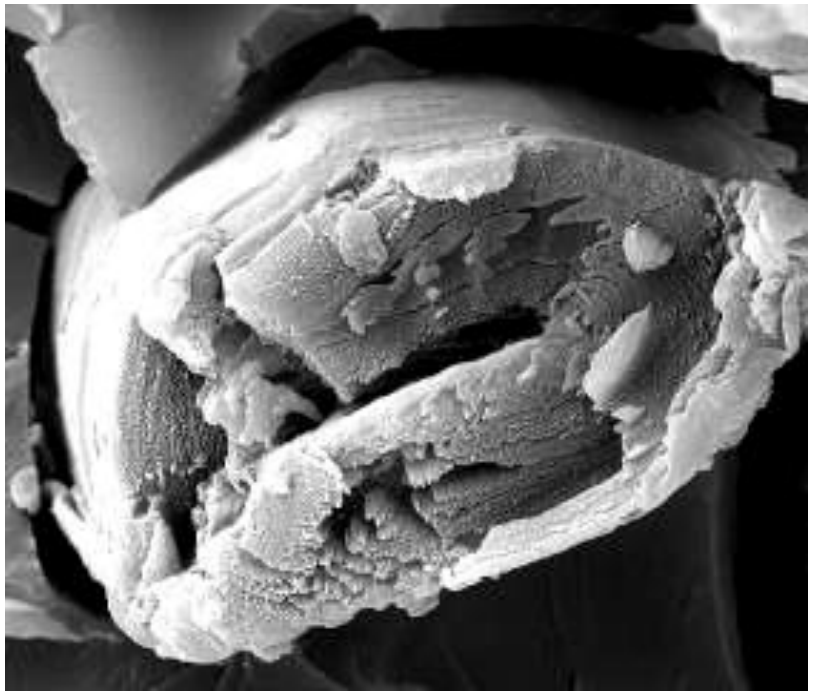


Ramie, native to China, is an important fiber crop in China since ancient times with a planting history of longer than 4700 years. At present there are approximately 4,000,000 Chinese acres of grass sown area of ramie, producing over 90% ramie output worldwide.

Ramie fabric was listed as by all previous dynasties Goinbo, became valuable thing which the imperial family and the high official aristocrat liked.

Ramie Fiber For Reinforcement

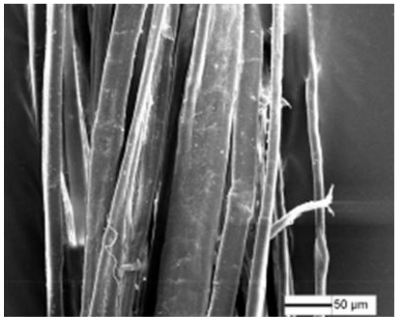




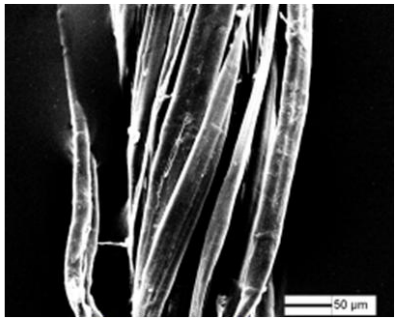
SEM micrographs of fractured surfaces of a ramie fiber embedded in epoxy

Li Y., Hu Y.P., Hu C.J. and Yu Y.H., Microstructures and Mechanical Properties of Natural Fibers, Advanced Materials Research, Vol. 33-37, 2008, 553-558

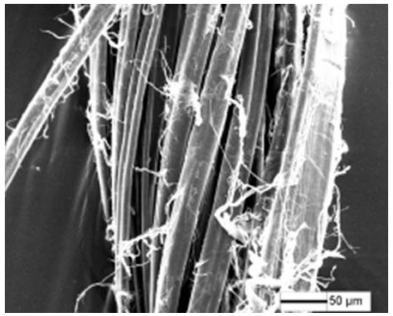
Interface, the Key Factor For the Application



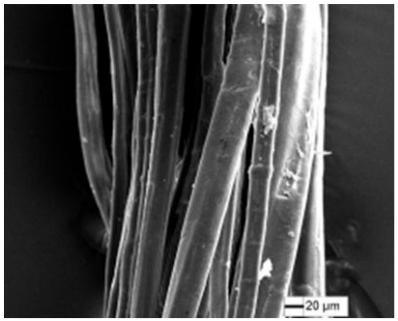
KMnO4



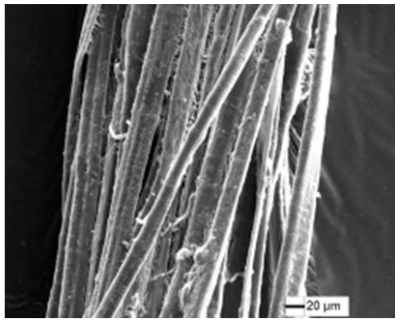
Fire retardant



As received

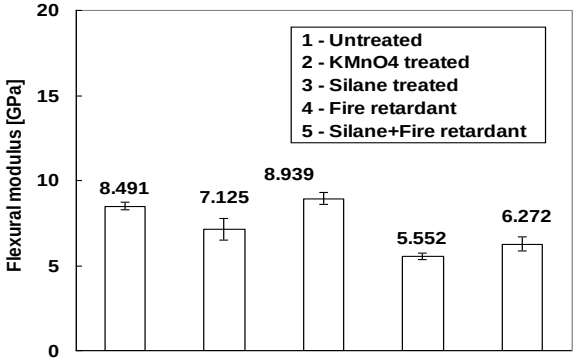


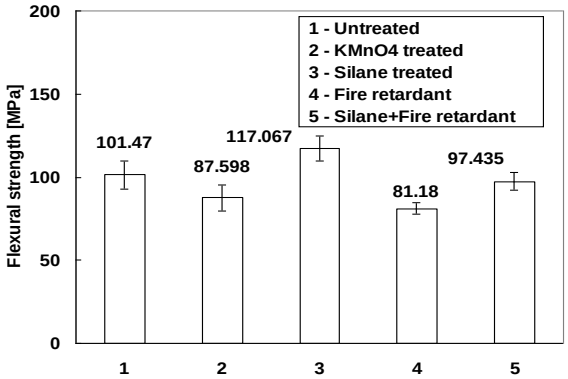
NaOH



Silane

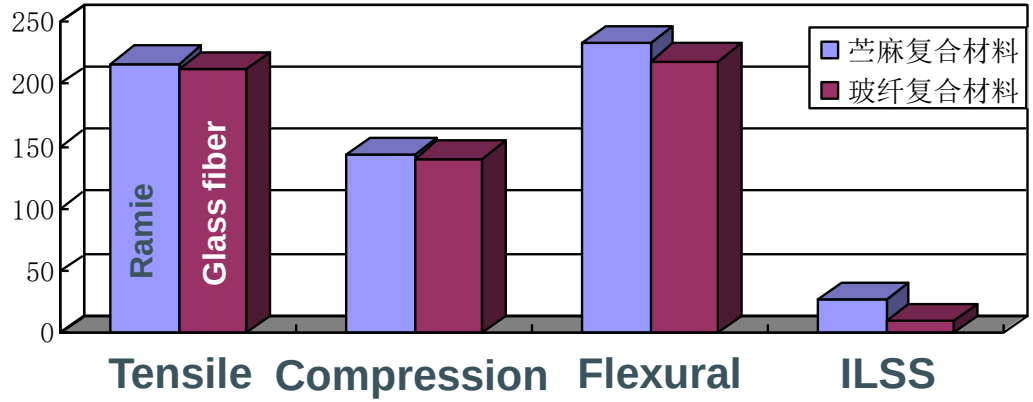
Ramie fiber
~ 70 vol%
phenolic resin
= GP4141





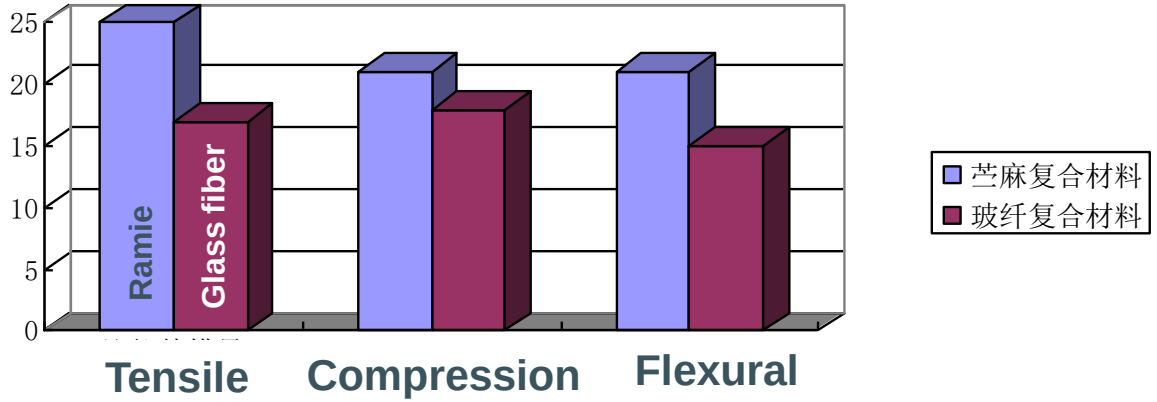
Li Y., Hu Y.P., Hu C.J. and Yu Y.H., Microstructures and Mechanical Properties of Natural Fibers, Advanced Materials Research, Vol. 33-37, 2008, 553-558

Specific Mechanical Properties with Phenol Resin

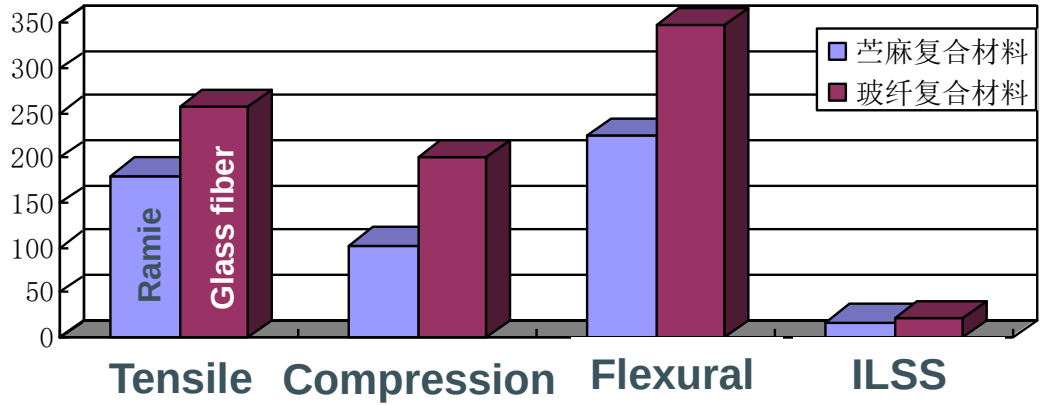


Specific Tensile Strength

Specific Tensile Modulus

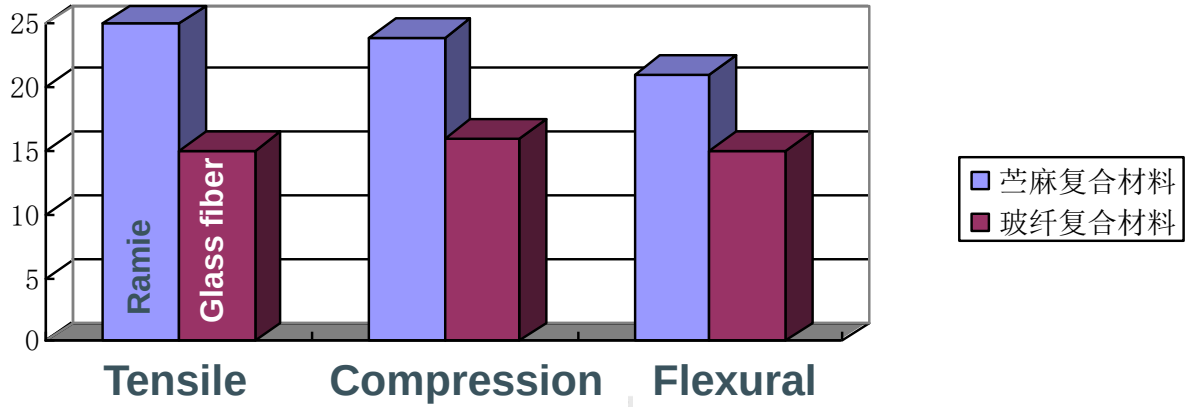


Specific Mechanical Properties with Epoxy Resin



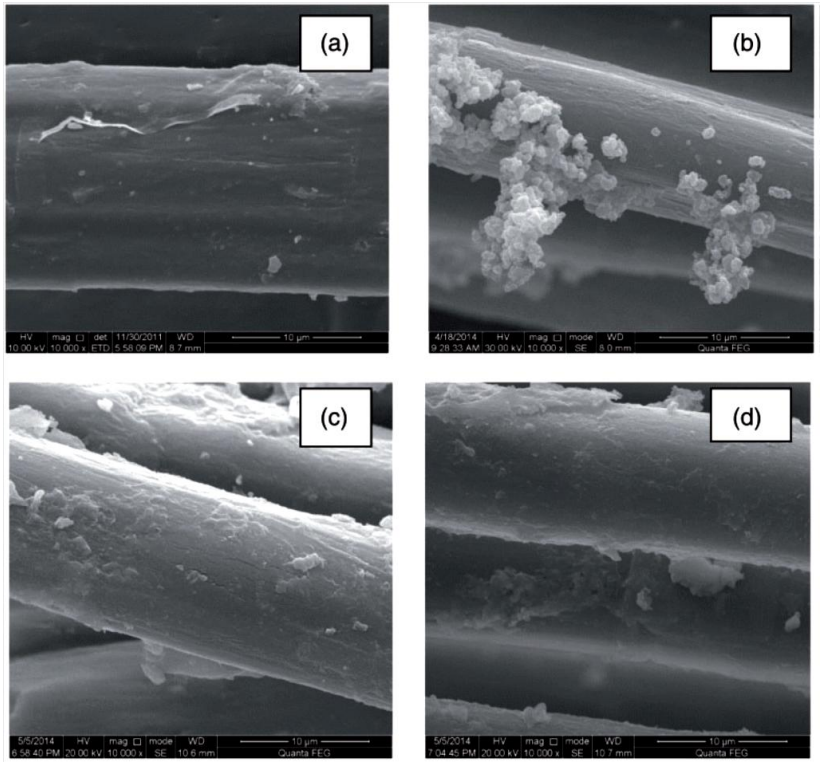
Specific Tensile Strength

Specific Tensile Modulus



Improvement of the Interfacial Bonding

- Nanoparticles ($ZrO_2.nH_2O$) on the flex fiber surface (b) in a remarkably agglomerated form. In comparison with it, grafting assisted with stirring (c) or sonification (d) resulted in more homogenous nanoparticle formation patterns.
- Attributed to the fact that stirring and sonification mixing promote the deposition of $ZrO_2.nH_2O$ particles on fiber surfaces, resulting in reduced particle agglomeration.

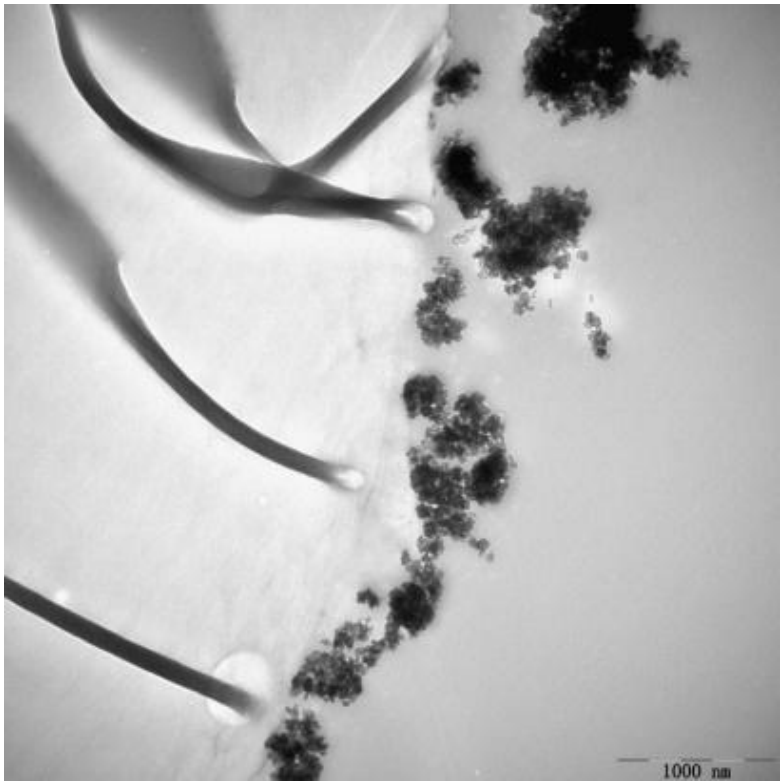


SEM images of surfaces of (a) control flax fibers, (b) fibers grafted under non-stirring conditions, (c) fibers grafted with mechanically stirring, and (d) fibers grafted via ultrasound sonication

Wang, H., G. Xian, and H. Li, Grafting of nano-TiO_2 onto flax fibers and the enhancement of the mechanical properties of the flax fiber and flax fiber/epoxy composite. Composites Part A: Applied Science and Manufacturing, 2015. 76: p. 172-180

Microscopic Study

- **TEM photograph of a cross section of a flax fiber grafted with $ZrO_2.nH_2O$ particles via ultrasonic.**
- **The $ZrO_2.nH_2O$ particles were grafted onto the FF surfaces in aggregation, and the diameter of the fine particles can be measured in nanometers.**



The left-hand image presents a cross section of the FF and of cracks formed during slicing. The black particles are nanoparticle aggregations

Wang, H., G. Xian, and H. Li, Grafting of nano-TiO_2 onto flax fibers and the enhancement of the mechanical properties of the flax fiber and flax fiber/epoxy composite. Composites Part A: Applied Science and Manufacturing, 2015. 76: p. 172-180

Single Fiber Tensile Test for the Control and Grafted FF

Samples	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
Control Fiber	399.7	30.4	1.56
Fiber grafted with non-stirring	512.9	32.8	1.82
Fiber grafted with mechanically Stirring	450.3	29.2	1.43
Fiber grafted with sonication	723.4	33.6	1.69
Fiber treated with sonication	428.8	30.2	1.57

Wang, H., G. Xian, and H. Li, Grafting of nano-TiO_2 onto flax fibers and the enhancement of the mechanical properties of the flax fiber and flax fiber/epoxy composite. Composites Part A: Applied Science and Manufacturing, 2015. 76: p. 172-180

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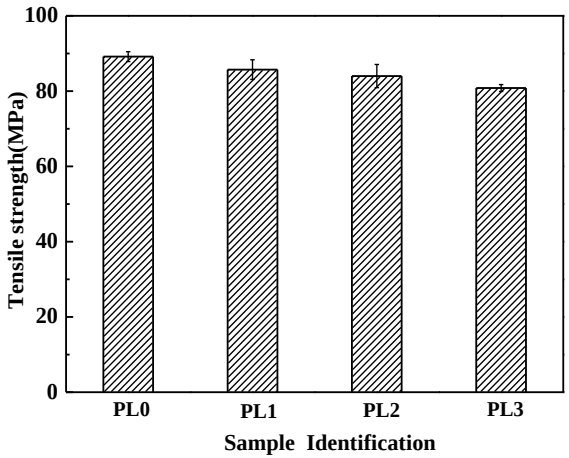
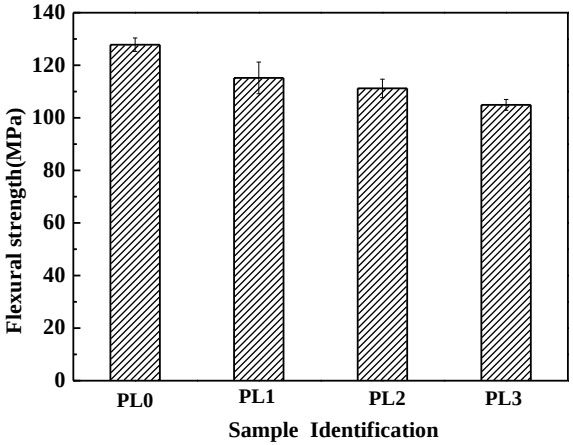
Flammability Study

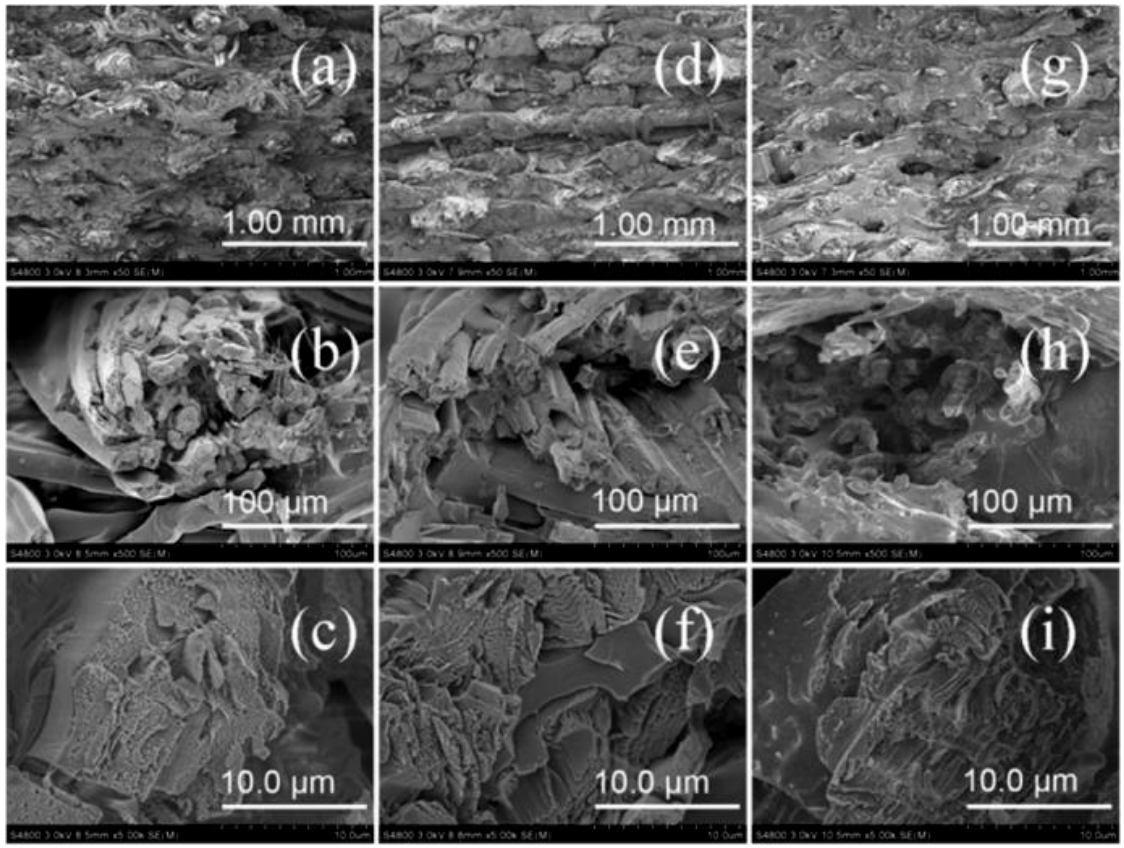




PL (wt%)	LOI (%)	UL94 Rating
0	39	VO
1	53	VO
3	65	VO
5	80	VO

- Test samples: Ramie fiber ~ 70 vol %, phenolic resin = GP4141
- With increased fire retardant, the LOI increases whereas the tensile and flexural strength decreases accordantly.

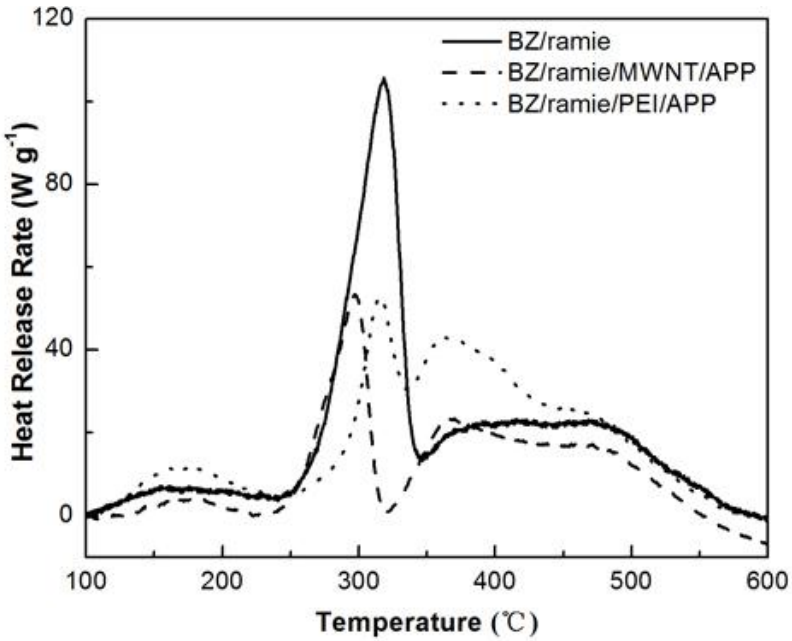
SEM Images of Fracture Surfaces of Benzoxazine Composites

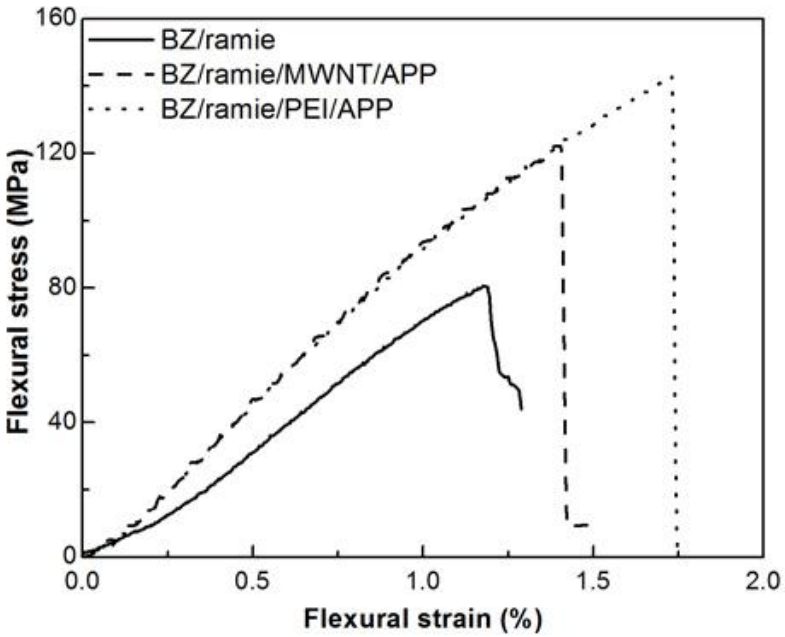


Zhang T, Wang LL, Yan HQ, Fang ZP. Construction of flame retardant coating on ramie fabric via layer-by-layer assembly and its application in polybenzoxazine laminate, The third Grubbs Symposium-Polymers and Green Industry, Ningbo, China, 2014.4.18-20

- BZ/ramie (a, b, c), BZ/ramie/MWNT/APP (d, e, f) and BZ/ramie/PEI/APP (g, h, i) laminates
- Intumescent multilayer nano-coatings not only improve fabric flame retardancy levels but also enhance interfacial adhesion between fabrics and certain polymer matrices.
- Fiber pull out effects disappeared after surface treatments were applied to the fractured composite surface

Simultaneous Improvement of The Properties



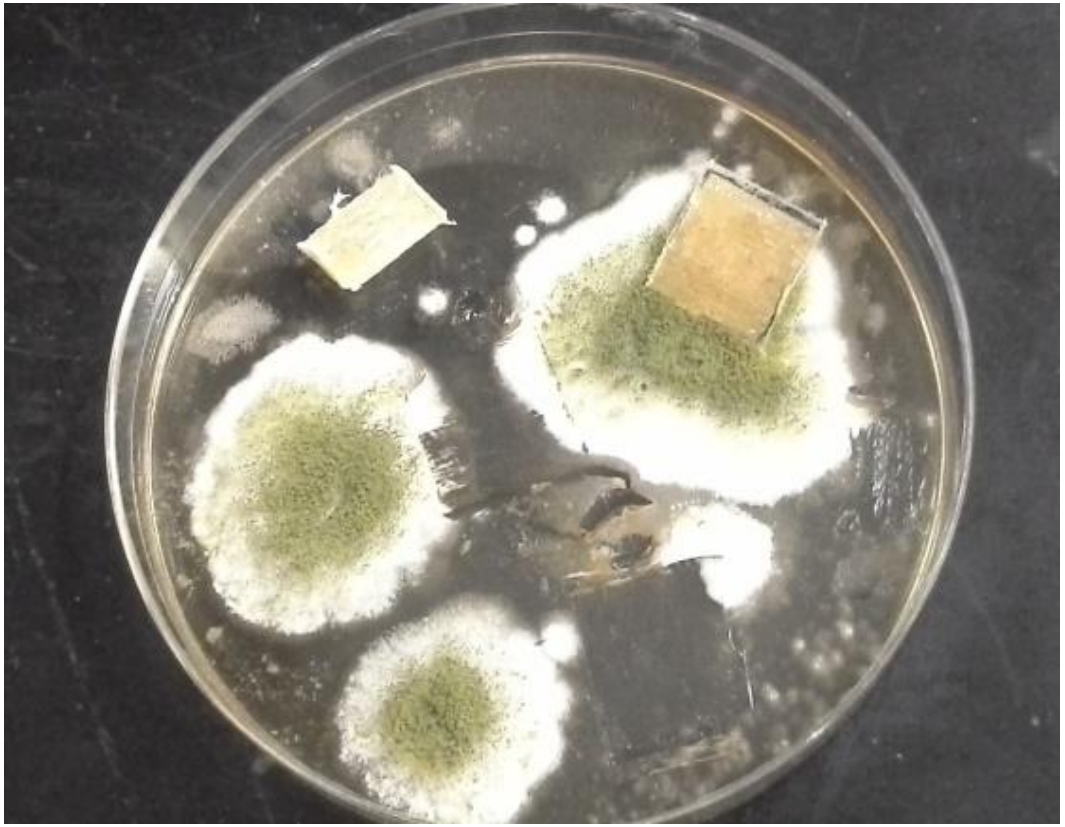


Heat release rate curves (l) and flexural stress levels vs. strain curves (r) for benzoxazine resin/ramie fabric laminates

Zhang T, Wang LL, Yan HQ, Fang ZP. Construction of flame retardant coating on ramie fabric via layer-by-layer assembly and its application in polybenzoxazine laminate, The third Grubbs Symposium-Polymers and Green Industry, Ningbo, China, 2014.4.18-20

Study on Antimicrobial Activity of ZrO_2 in Composite

- In the control, a significant expansion of fungal colonies was observed throughout the composite, whereas in the modified samples, almost no colony growth was found. This reveals the antifungal activity of ZrO_2 nanoparticles*.
- Thus, composites with significant antimicrobial properties are expected to exhibit long-term stability features.



Khan BA, Warner P, Wang H, Antibacterial Properties of Hemp and Other Natural Fibre Plants: A Review. *Bioresources* 2014; 9(2):3642-3659.

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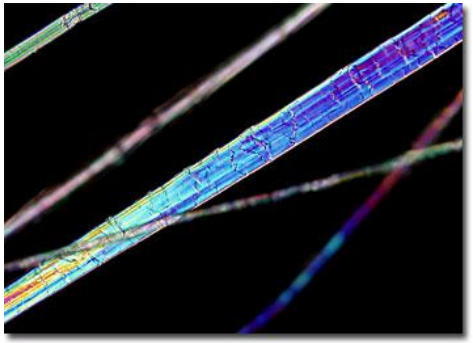
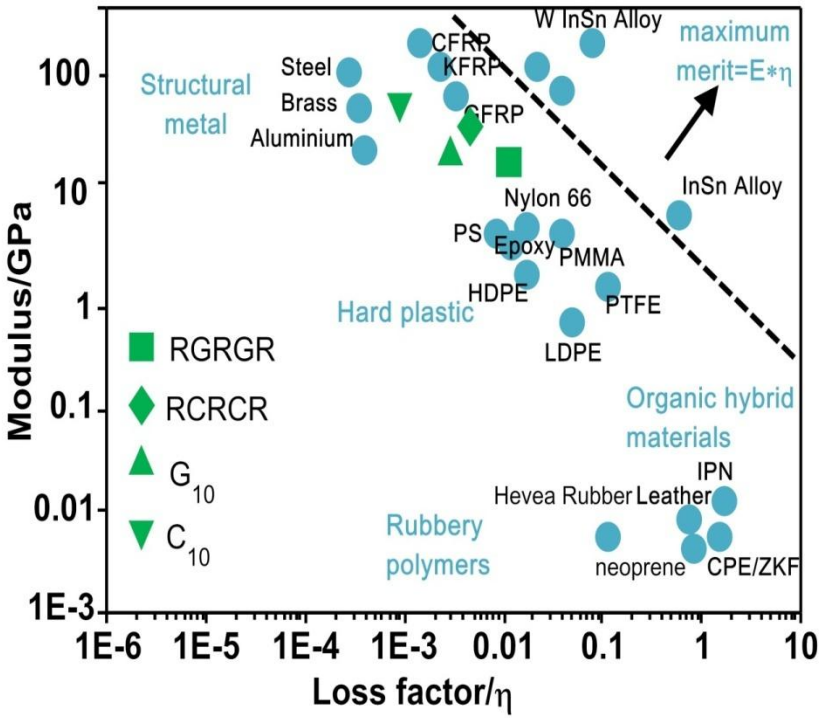
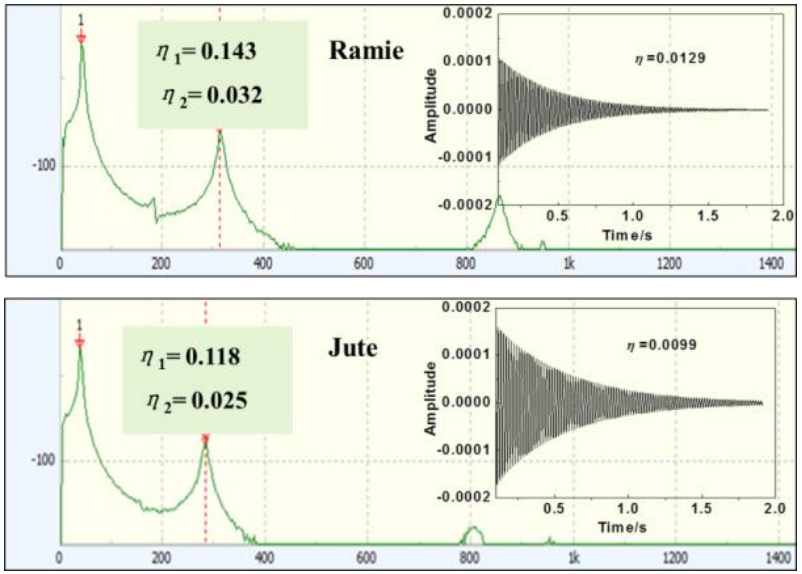
Structural Damping Functionality of the Biocomposite

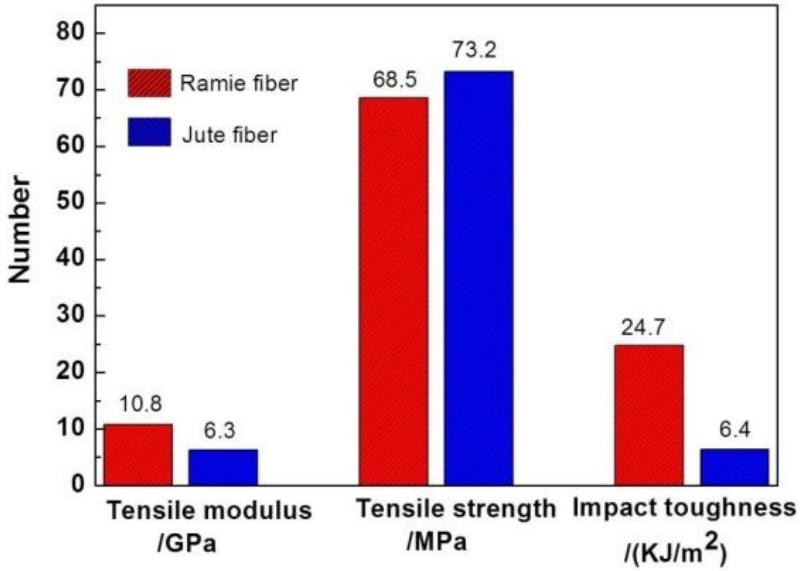
- Unique low density + damping properties due to the porous microstructures





Structural Damping Behavior in Comparison





- A ramie laminate loss factor (η) of 0.0129 for the free vibration condition, which is over 30% higher than that of the jute laminate of 0.0099, whereas in the forced vibration condition, η values of the first and second order are 0.143 (η_1) and 0.032 (η_2), respectively, for the ramie and 0.118 (η_1) and 0.025 (η_2), respectively, for the jute.
- These results suggest that ramie may exhibit higher levels of damping efficiency than jute, though both maintain their inherent structural properties

N.Ni, Y.Wen, D.He, XS.Yi, et al, High damping and high stiffness CFRP composites with aramid non-woven fabric interlayers. Compos.Sci.Technol. 117 (2015) 92-99

Comparison Between Physical and Mechanical Properties of the Neat and Hybrid Laminates

	Density (g/cm^3)	Loss factor	Tensile strength (MPa)	Tensile modulus (GPa)	Interlaminar shear strength (MPa)	Elongation at break (%)	Impact toughness (kJ/m^2)
R10	1.35	0.0129	68	11	21	0.6	24.7
G10	1.73	0.0042	481	20	71	2.4	220.7
GRGRG	1.59	0.0043	322	15	59	2.2	138.4
RGRGR	1.51	0.0101	278	10	36	2.84	116.4
C10	1.53	0.0018	888	61	88	1.3	104.4
CRCRC	1.49	0.0024	596	40.2	50	1.5	86.2
RCRCR	1.40	0.0057	382	21.3	32	1.1	55.0

N.Ni, Y.Wen, D.He, XS.Yi, et al, High damping and high stiffness CFRP composites with aramid non-woven fabric interlayers. Compos.Sci.Technol. 117 (2015) 92-99

Application in Music Instruments and Sport Articles

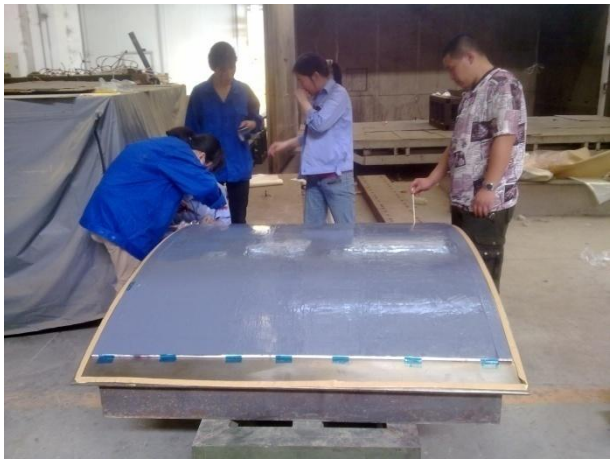
Yi XS, et al. *PCT Patent* in pending

Outline

1. Why to jointly develop green composites for aviation?
2. Bio-sourced resins as matrices and plant fibers as reinforcing component for biocomposites
3. Special problem with biocomposites: flame retardation and hygrothermal stabilization
4. Trial application and demonstration
5. Conclusions and outlook

Trial Application and Demonstration

- Manufacturing of an acoustic panel in a ramie/glass/EP hybrid-laminated design



Yi XS, et al. *PCT Patent* in pending

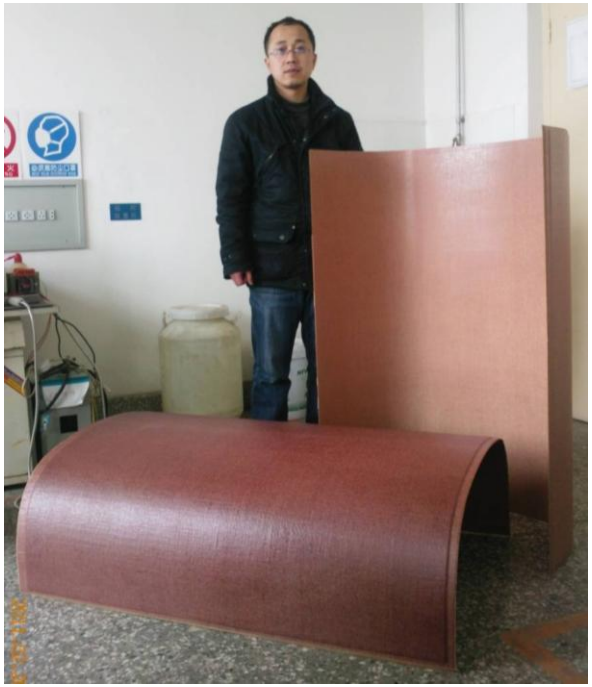
Trial Application and Demonstration

- Manufacturing of an acoustic panel in a ramie/glass/EP hybrid-laminated design

Yi XS, et al. *PCT Patent* in pending

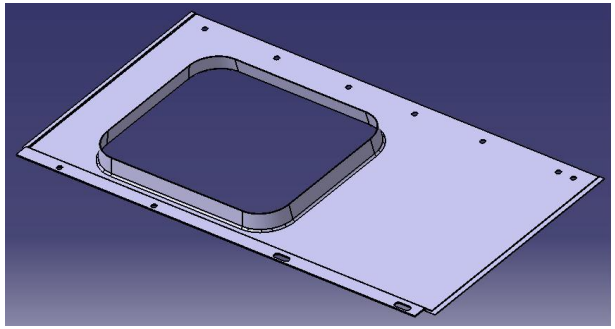
Trial Application and Demonstration

- Sandwich panels with plain-woven ramie as face sheets impregnated with phenol and with Nomex honeycomb as the core



Yi XS, et al. *PCT Patent* in pending

Trial Application and Demonstration



Yi XS, et al. *PCT Patent* in pending

Trial Application and Demonstration

- Proof-of-concept demonstration of a decorative, quasi-structural composite side-panel produced with ramie fabric as the surface layer of a railcar

Yi XS, et al. *PCT Patent* in pending

Trial Application and Demonstration

- Application of decorative, function-integrated composite panels to the interior of a seaplane

Yi XS, et al. *PCT Patent* in pending

Conclusions

1. Bio-sourced polymers, natural fiber reinforcements and biocomposites have continuously been studied and developed worldwide. However, environmental and resource-related benefits of these new materials are still compromised by limited technical performance and material life properties.
2. The development goal is to advance material technologies and to effectively apply novel composites to aircraft, rail transportation and civil engineering settings. This involves adapting materials and processes to state-of-the-art composite standards.
3. The development of function-integrated PFRC structure appears to be more essential and feasible than that of mere “high-performance” biocomposites. Typical cases pertaining to structural damping and decorative quasi-structural composites have been presented.

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THANK YOU FOR YOUR ATTENTION.