THE FUEL AND ENERGY RESEARCH FORUM

Aston University
Engineering & Applied Science

Recovery and Application of Waste Carbon Fibre Reinforced Plastics (CFRP)

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Biomass and Waste/Fuel Characterisation, upgrading and Carbonisation Interest Group Seminar and Annual General Meeting

Wednesday 10th April 2019

Aston University, Birmingham, UK

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Introduction

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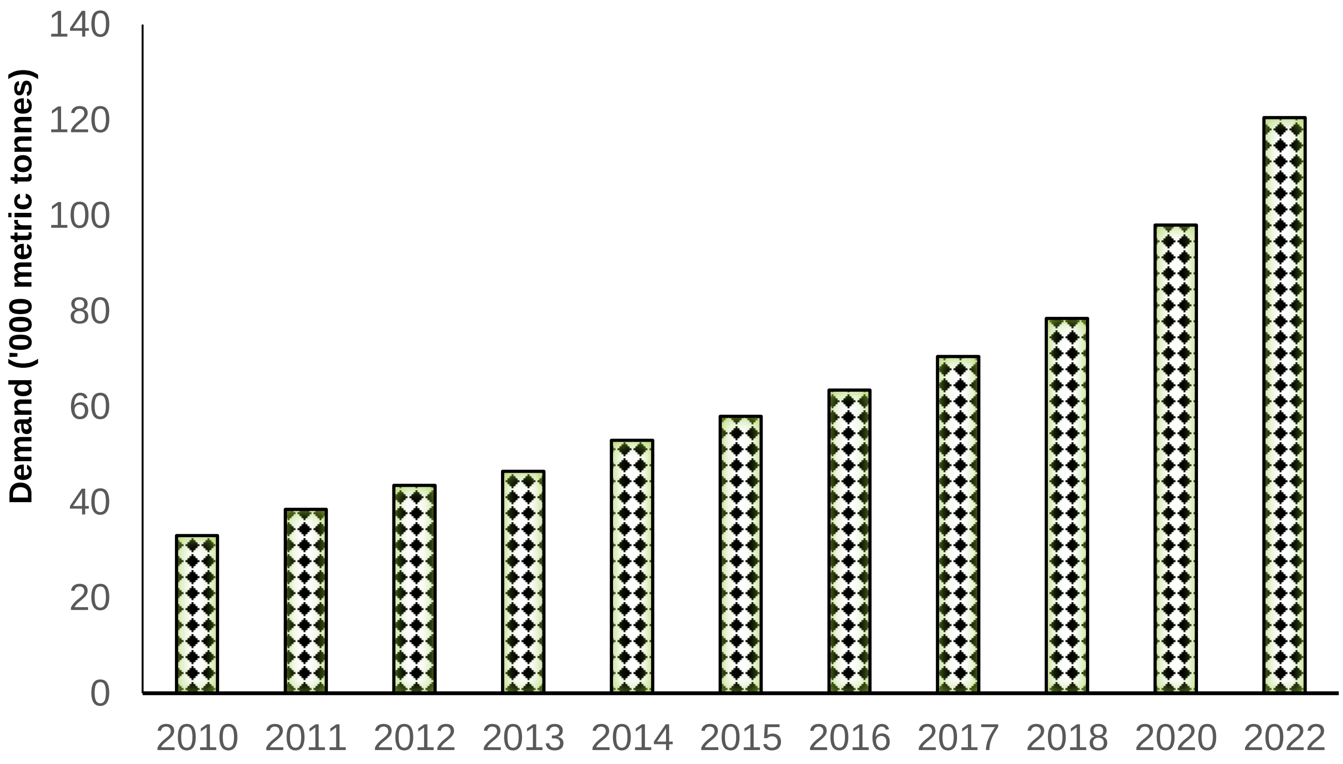
The worldwide demand for carbon fibre was 38000 tonnes in 2010 and expected to rise to 125000 tonnes by 2020[1]



1. Tony, R., 2011. The Carbon Fibre Industry Worldwide 2011-2020: An Evaluation Of Current Markets And Future Supply And Demand. Materials Technologies Publications.

Properties of Carbon Fibre

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Carbon fibre is made of honeycomb-shaped carbon crystals aligned in a long axis in flattened ribbons (mainly from PAN (90%) and rayon)

- ✓ Fire Resistance/Not flammable
- ✓ High Thermal Conductivity in some forms
- ✓ Low coefficient of thermal expansion
- ✓ Non-toxic
- ✓ Biologically inert
- ✓ X-Ray Permeable
- ✓ Relatively Expensive

- ✓ High Strength to weight ratio
- ✓ Rigidity
- ✓ Corrosion resistance
- ✓ Electrical Conductivity
- ✓ Fatigue Resistance
- ✓ Good tensile strength but Brittle

Uses and CFRP Waste Generation

- On a Boeing 787, 50% of the aircraft is composite, with 20% aluminium, 15% titanium, 10% steel and 5% other materials.
- About 60-70% of the structural weight of Formula One cars (e.g. McLaren Formula 1 – A)
- Other aerospace e.g. satellite bodies
- Sports equipment – tennis rackets, golf clubs
- Between 6000 to 8000 airplanes expected to reach their end of service life, which will generate CFRP wastes, by 2030[2]

2. Vicki P, M. (2010). "Launching the carbon fibre recycling industry." Reinforced Plastics 54(2): 33-37

Disposal of Waste Carbon Fibres

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Currently, about 3000 tonnes of CRFP waste is generated annually in Europe and UK.

Landfilling is not a good option – loss of valuable material and carbon fibre is non-putrescible

Incineration is not a good option – carbon fibre is flame retardant, hence large quantities of fuel would be required for its incineration

Often used as reinforcements for plastics with thermosetting resins as binding agents

Reuse and recycling appear to be viable solutions

Main Routes for Recycling

Mechanical – bulk ball milling + air-classification

Thermal – mostly combustion and pyrolysis; removes resins and plastics for energy recovery

Chemical – to remove resins and plastics

- Solvolysis (hydrolysis, Glycolysis, Alcoholysis)

Research Aims & Objectives

Aims

- Recovery of carbon fibres from the waste with minimal impact on physical properties for re-application

- Recovery of the resin as monomers (valuable chemical feedstock) or as fuel

Objectives

- The effect of solvents, temperature, type of catalyst and reaction time on resin removal efficiency

- Manufacture of composite materials and testing them

Materials

CFRP wastes supplied by ELG Carbon Fibre Ltd

Elemental Composition of Waste CFRP

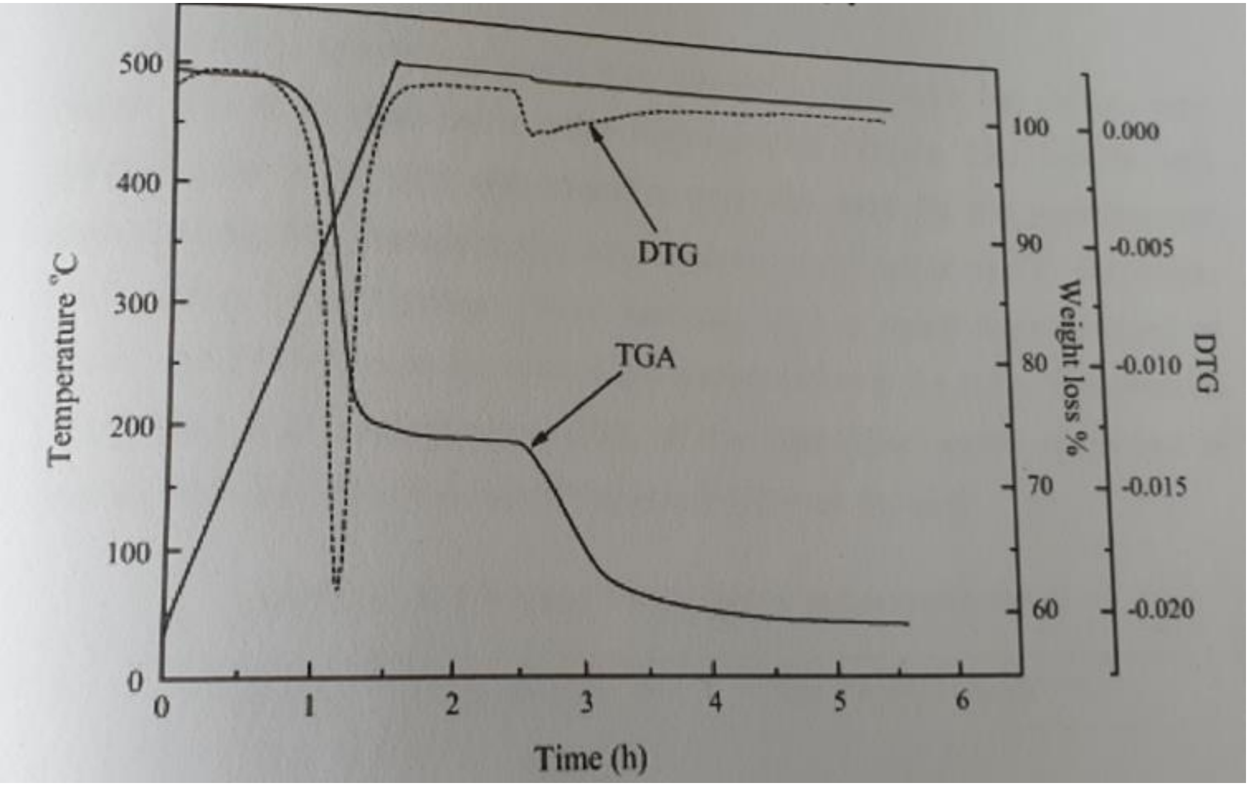
	C	N	H	S	O
CFRP waste	**80.3**	**4.15**	**2.05**	**1.65**	**6.9**

Water and Ethylene Glycol (EG) used as solvent

Solvothermal experiments at temperatures 380-400 ^{o}C

Annually, about 2.6 billion litres of waste ethylene glycol is generated in the US alone; a large proportion of this comes from de-icing of aeroplanes and from spent heat transfer fluids

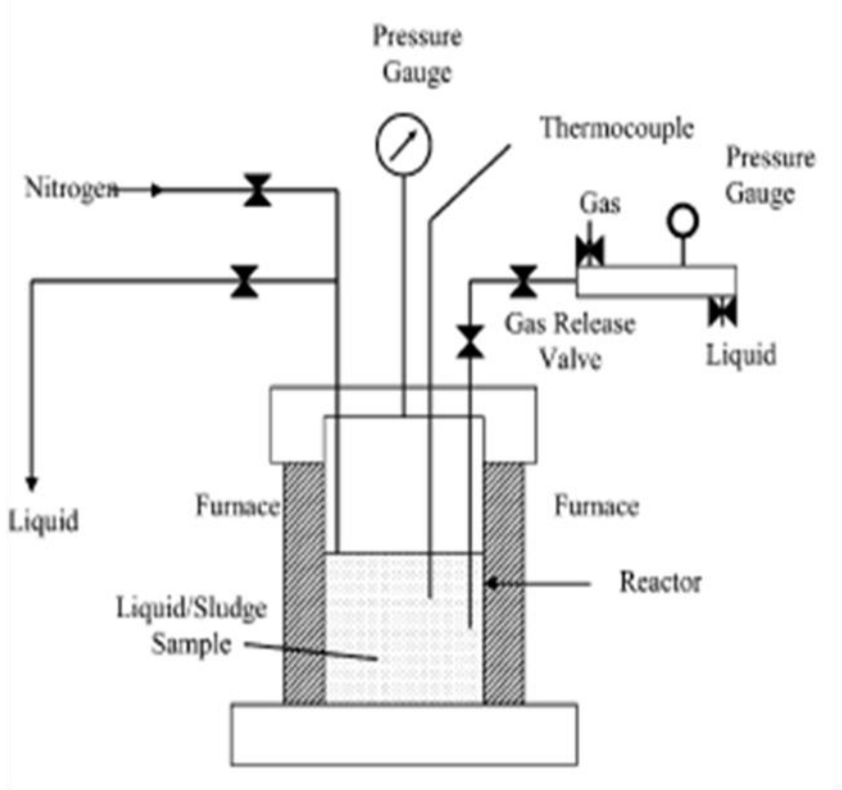
Characterisation of Waste CFRP



- ❖ On average, CFRP consisted of 38.5 wt% of resin and 61.5 wt% of carbon fibre by TGA characterisation and ASTM D3174 – 12 ashing method.
- ❖ Virgin carbon fibre contained 99.5 wt% carbon fibre

Experimental

- SS316 batch reactor obtained from the Parr Instrument Co., USA,
- 10 g of CFRP in 60 ml of solvent (EG/water)
- Gas analysis in Varian CP-3380 (GC/TCD & GC/FID)
- Liquid analysis in TOC for total carbon content.
- Solid characterisation



Product distribution with H_2O/EG systems

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Sample No	H_2O, mL	EG, mL	T, ºC	*Liquid, %	Gas, %	Solid, %	Resin removal %
1	0	60	380	88.7	2.16	9.05	79.30
2	0	60	400	88.4	3.16	8.41	92.1
3	10	50	380	87.4	4.22	8.42	94.2
4	10	50	400	89.2	2.58	8.25	97.6
5	15	45	400	86.3	5.31	8.44	95.2
6	30	30	400	84.4	5.88	9.75	73.8
7	45	15	400	84.0	5.68	10.4	66.5
8	50	10	400	88.1	1.30	10.6	67.3
9	60	0	400	89.1	0.69	11.6	49.0

*weight % of solvent(s) + liquid products by difference

Yildirir E, **Onwudili JA**, Williams PT, **J. Supercritical Fluids** 92, 107-114. 2015.

Organic products in liquid residuals

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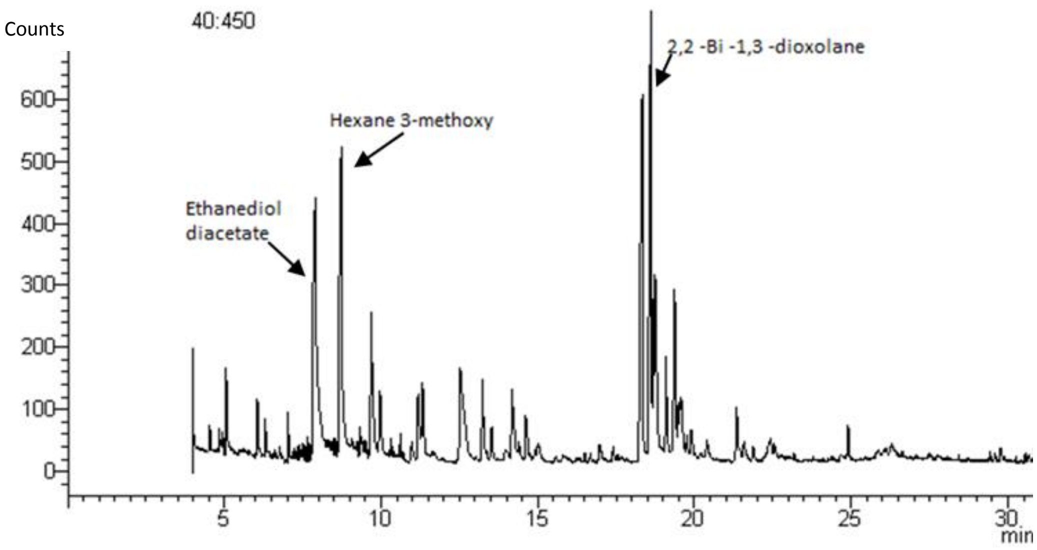
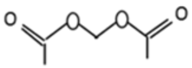
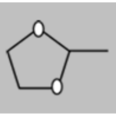
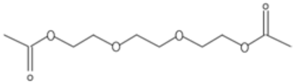
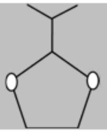
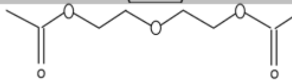
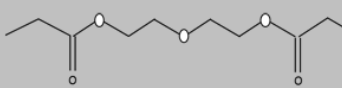
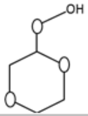
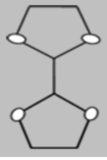


GC/MS/MS outline of liquid obtained from CFRP test at 400 ºC with EG only (acidic extraction)

	Organic compounds detected with ethylene glycol as solvent	
S/N	Compound	Structure
1	1,1-Ethanediol diacetate	
2	2-Methyl-1,3-Dioxolane	
3	Ethanol, 2,2'-[1,2-ethanediylbis(oxy)] bis, diacetate	
4	2-(1-Methylethyl)-1,3-Dioxolane,	
5	Ethanol, 2,2'-oxybis-, diacetate	
6	Ethanol, 2,2'-oxybis-, dipropanoate	
7	Hydroperoxide, 1,4-dioxan-2-yl	
8	2,2'-Bi-1,3-dixolane	

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Mechanical properties of virgin and recovered fibre

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	Recovered CF		
	*Virgin	1	2
Breaking Force, N	0.135	0.138	0.131
Elongation, mm	0.3	0.28	0.43
Tensile Strength, GPa	3.5	3.6	3.4
Young Modulus (MPa)	233	254	159

1 Recovered at 400°C, with 10 ml of H2O, 50 ml of EG

2 Recovered at 400°C, with EG only

*Sourced in UK

Yildirir E, Miskolczi N, **Onwudili JA,** Németh NE, Williams PT, Sója J, Composites Part B: Engineering 78, 393-400. 2015

Materials for Composite Production

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Commercial LDPE (Bralen RB 2-62, Tisza Chemical Group Public Limited Company, Hungary)

Virgin Fibre

Properties	PANEX®33
Tensile strength, MPa	3800
Tensile modulus, GPa	228
Density, g/cm^3	1,81
Diameter, mm	7,2
Carbon content, %	95
Sizing	no

LDPE

Properties	Bralen RB 2-62
Tensile Strength, Mpa	11.4
Tensile Modulus, MPa	348
Tensile Extension, %	155
Flexural Strength, MPa	7.5
Flexural Modulus,MPa	495

Commercial additives (coupling agents):

- 3 – Amino – Propyl - Silane (silane-based additive)
- Grafted – Maleic Anhydride

Composite Making

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Two roll mill (Labtech Ltd, Thailand)

- First mill at 180 ºC; second mill at 150 ºC
- Press moulding at 180 ºC

Composite Making

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Ten samples of composite materials were prepared as follows:

	*Composite with Recovered Fibre					Composite with Virgin Fibre				
Compound (wt %)	**CFS-1**	**CFS-2**	**CFS-3**	**CFS-4**	**CFS-5**	**CFS-11**	**CFS-12**	**CFS-13**	**CFS-14**	**CFS-15**
LDPE	85	84	84	83	83	85	84	84	83	83
Recovered CF	15	15	15	15	15	-	-	-	-	-
Virgin CF	-	-	-	-	-	15	15	15	15	15
Silane based	-	1	-	-	-	-	1	-	-	-
grafted-MA	-	-	1	-	-	-	-	1	-	-
Ad-1	-	-	-	2	-	-	-	-	2	-
Ad-4	-	-	-	-	2	-	-	-	-	2

* CF recovered at 400 °C, with 10 mL of H_2O, 50 mL of EG

Onwudili JA, Miskolczi N, Nagy T, Lipóczi G, Composites Part B: Engineering 91, 154-161. 2016.

Composites Produced

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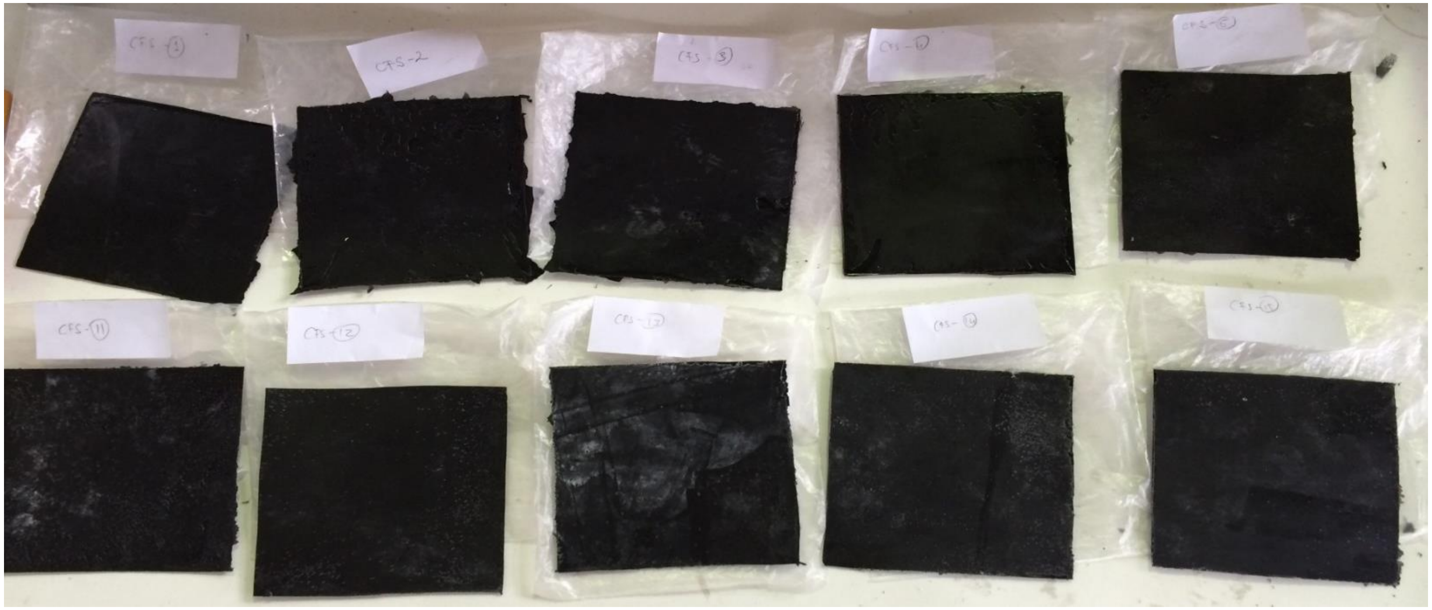

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Testing of Composites

Tensile properties on Instron 3345 testing machine (according to MSZ EN ISO 527-1-4:199 std)

Composites were cut into 10 x 1 x 100 mm

Charpy test on CEAST Resil Impactor according to MSZ EN ISO 179-2:2000 std mtd

Samples 6.5 mm deep V-form notch cut

Mechanical properties of virgin and recovered fibre

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- Breaking Force (N)
- Tensile Strength (GPa)
- Tensile Strain extension at maximum load (mm)
- Young's modulus (MPa) – stiffness test
- Flexural Properties
- Charpy (Impact Energy) Test

Also tested effect of the additives to the mechanical properties

Tensile Tests Results from Composites

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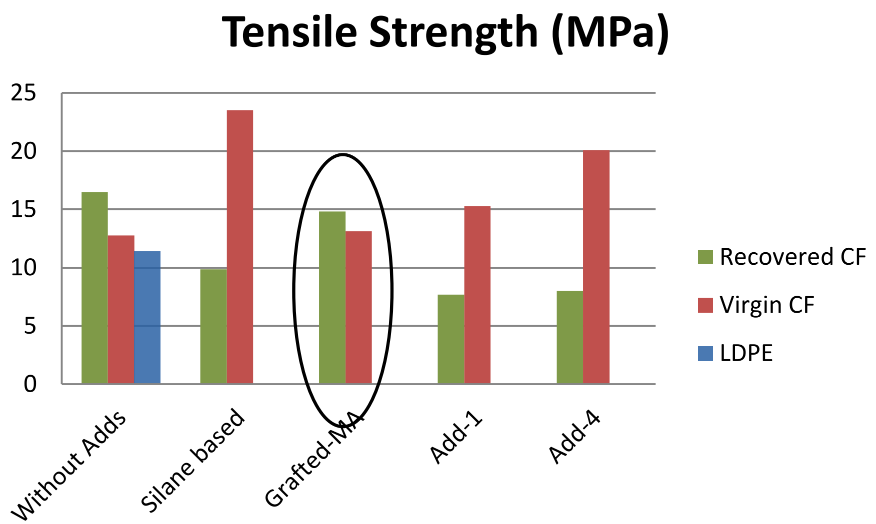

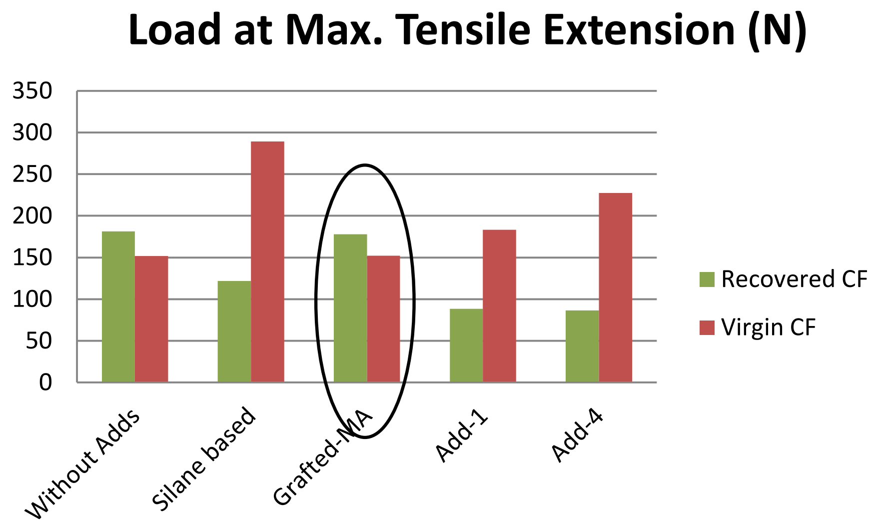

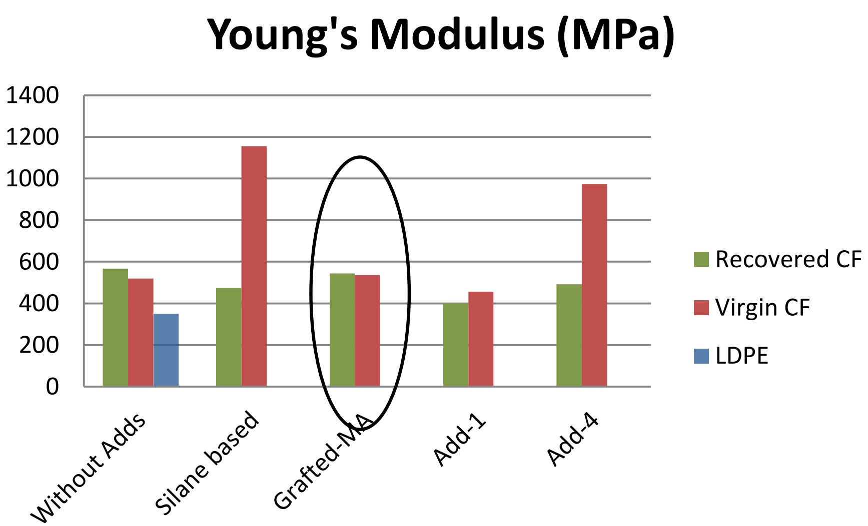

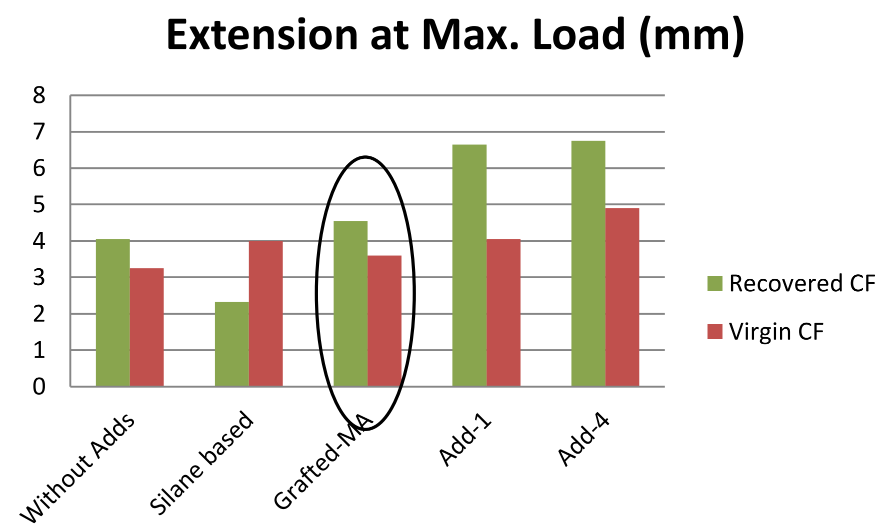

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Flexural Tests Results from Composites

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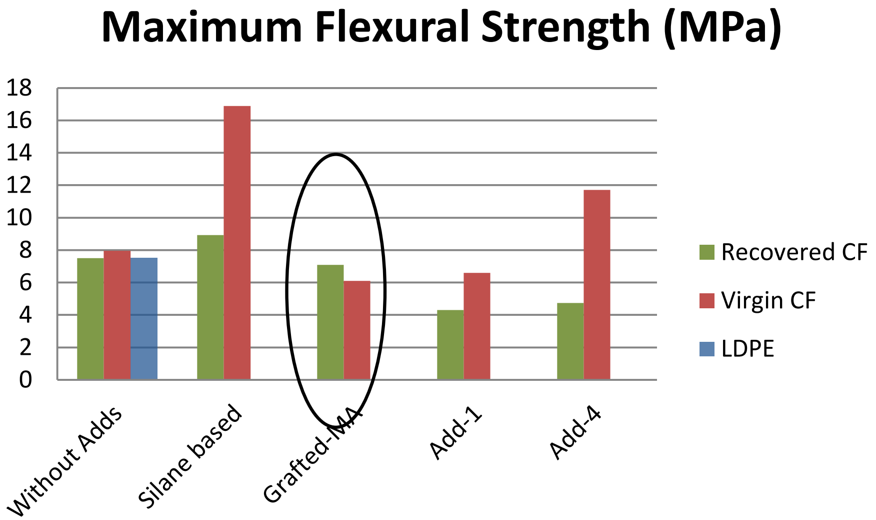

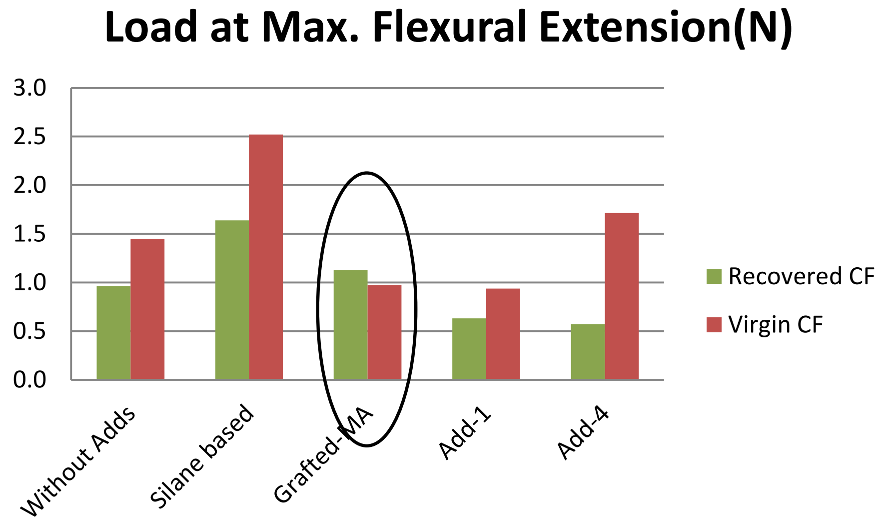

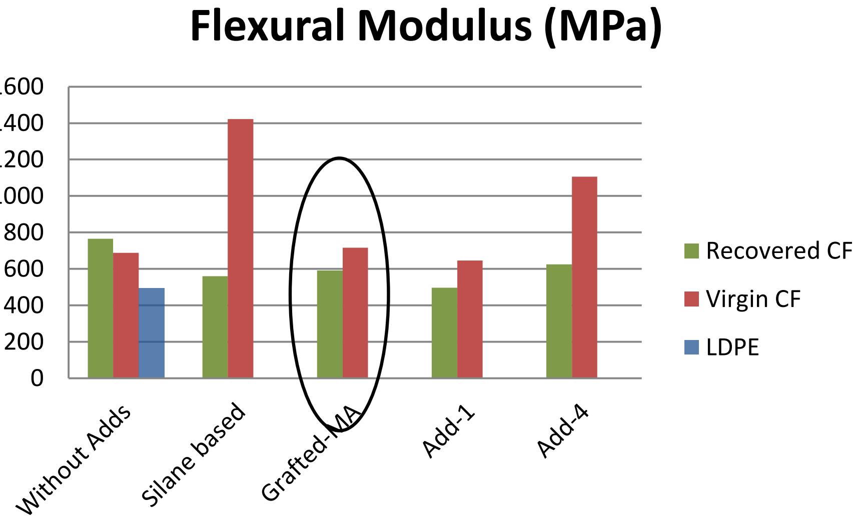

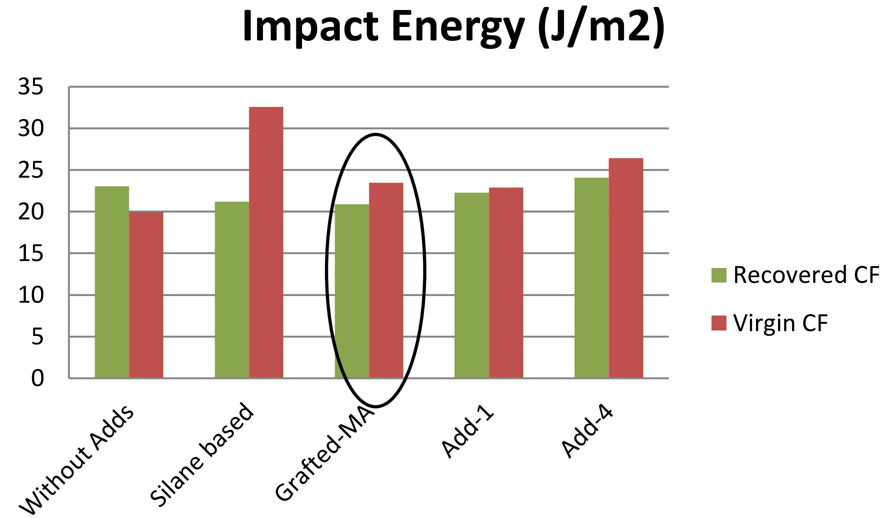

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Conclusions

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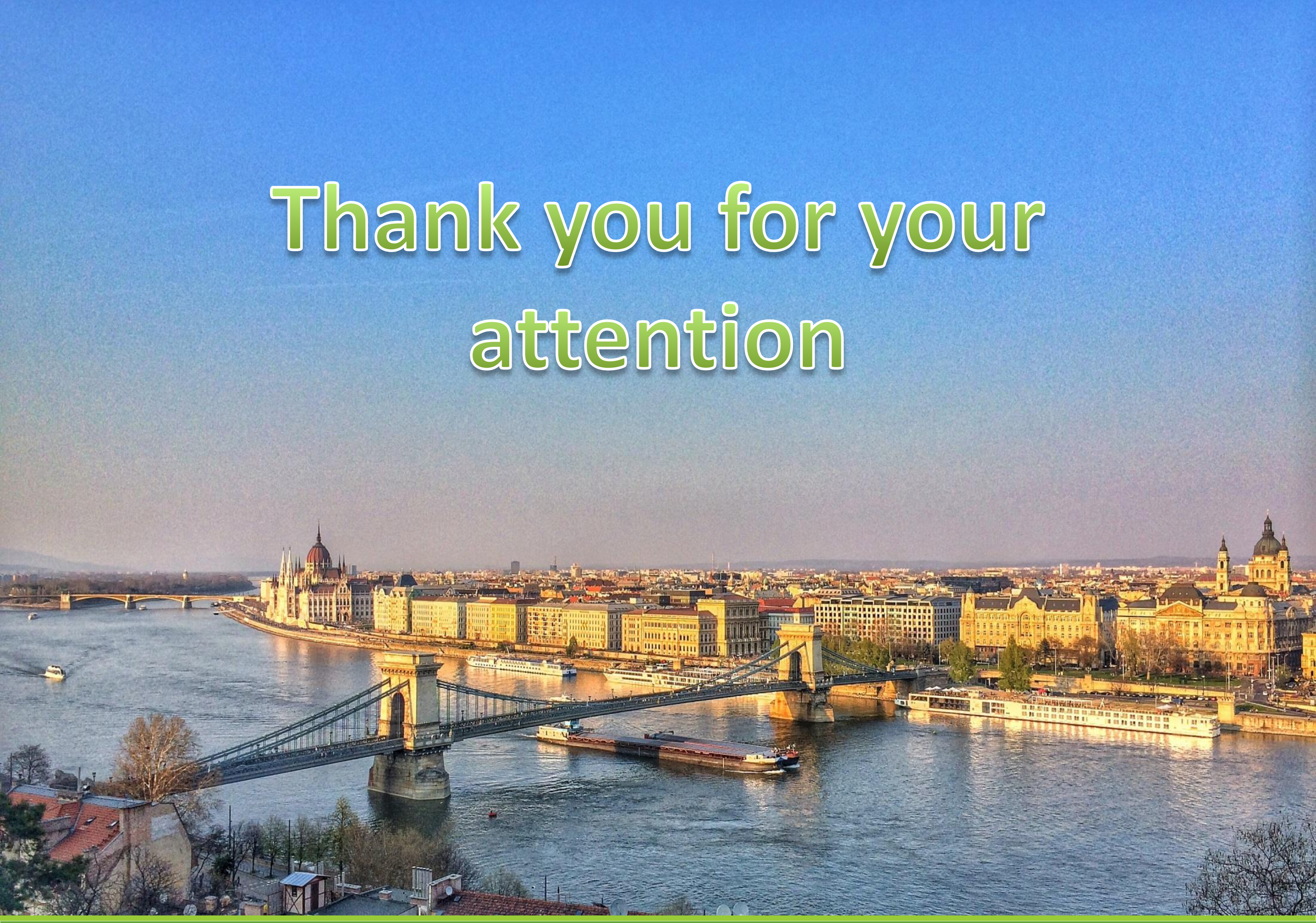
- Using water alone, a maximum of 49 wt% of resin was removed
- With EG alone, 92% of resin removal was reached, higher percentages were reached by using EG/water mixture
- The liquid residuals from EG-promoted process could be valorised into fuel gas by supercritical water gasification or refined into liquid fuel
- LDPE's mechanical properties were improved when reinforced with RCF
- The commercial additive (silane-based) did not work well with the RCF; maybe due to loss of surface active groups compared to VCF

Acknowledgements

Royal Society for International Exchanges Grant with University of Pannonia, Hungary

Dr Eyup Yildirir
Dr Norbert Miskolczi
Professor Paul T. Williams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