
spe
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COMPOSITES: Forming the Future
of Transportation Worldwide
SEPT 4-6, 2019

Synthesis & Properties of multifunctional epoxy resins containing naphthalene units

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Contents

- Introduction

  Applications of epoxy resin

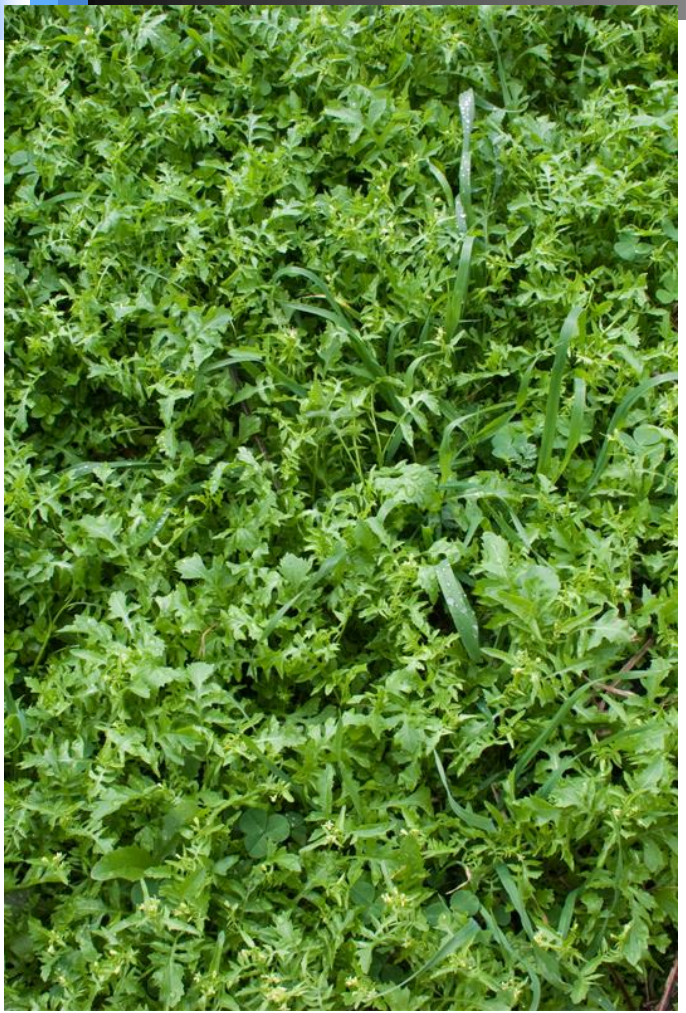
  Need for high thermal resistance, high modulus and excellent Hot-Wet properties.

- Our recent work

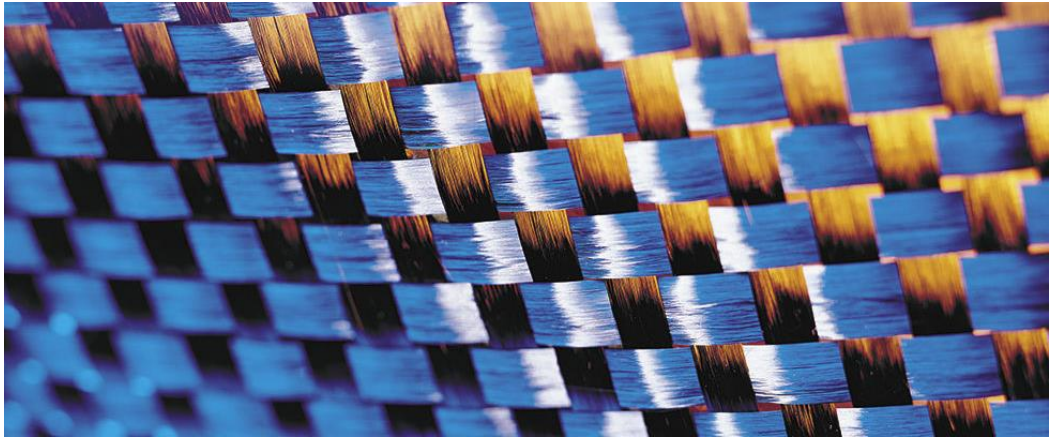
  Design of naphthalene type epoxy resin

- This work

  Synthesis and properties of new multi-functional epoxy resins containing naphthalene unit



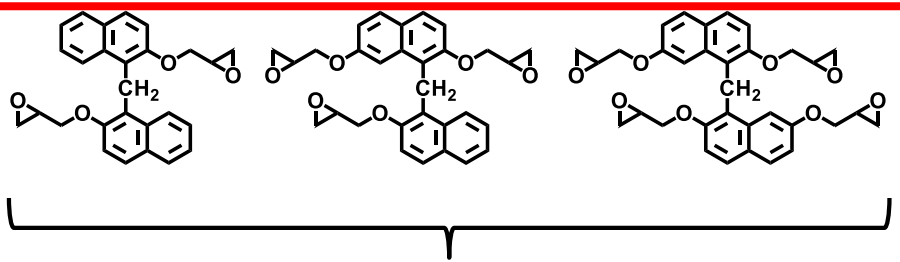
In the Weeds of Chemistry to Materials & Applications



Abstract

- We synthesized the new multi-functional epoxy resins containing Naphthalene unit.
- Cured resins exhibited high Tg, high modulus and excellent hot-wet properties suitable for composite and electronic applications.

The new epoxy resins



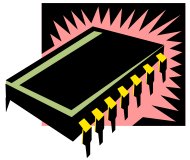
Combination with these chemical structures

Uses for Epoxy Resin

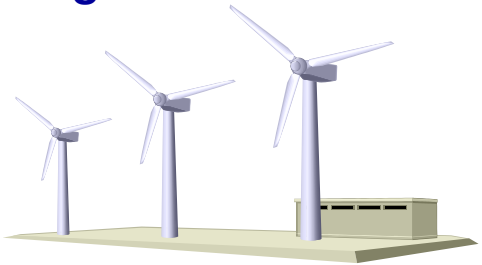
Applications

Coatings

Adhesives



Molding Compounds



Composite Materials

Aerospace

Industry Challenges

High Temperature Resistance (hot/wet)

Moisture Resistance

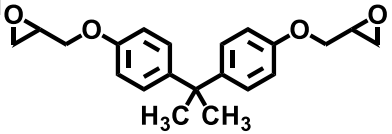
Time/Cure

Higher Quality Requirements

Mechanical Property Requirements

Conventional molecular design of high thermal resistance resin

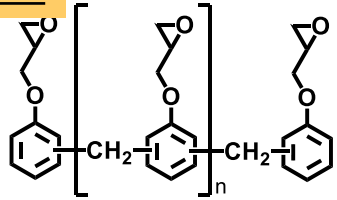
E-BPA



Di-functional type
(Standard)

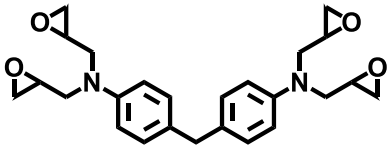
Poly-functional type (oligomer)

EPN



Tetra-functional type (oligomer)

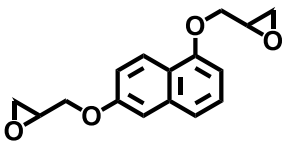
TGDDM



Molecular design of epoxy resin with Naphthalene unit

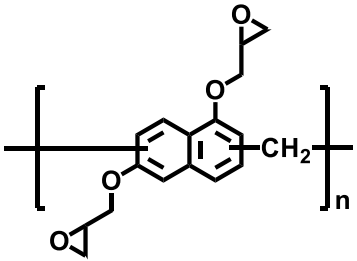
Naphthalene type (recent work)

E-DHN



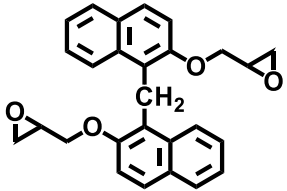
- High modulus
- High flexural strength
- Liquid state (but may cause crystallization)

E-DHNN



- High modulus
- Solid state
- High melt viscosity

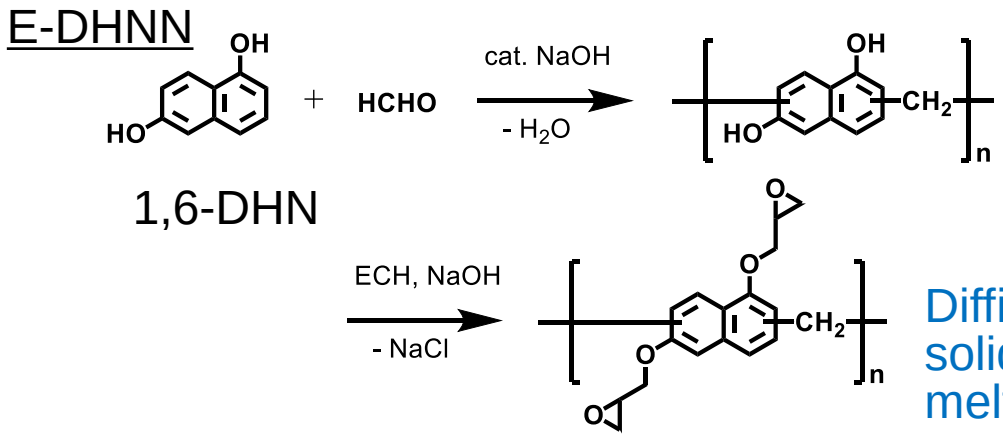
E-2HND



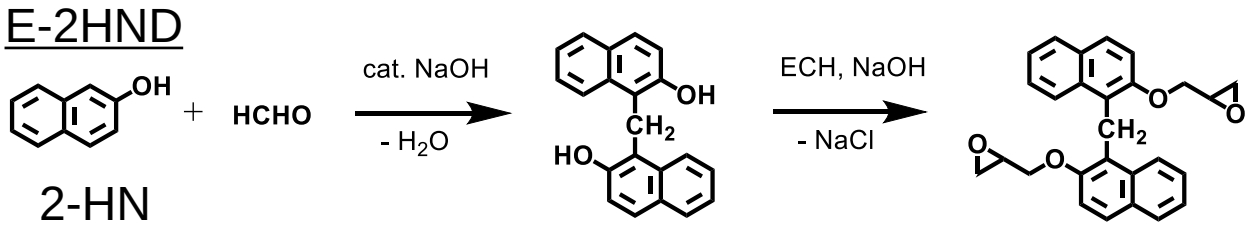
- High modulus
- Crystalline state (melting point is more than 200℃)

This chemical structure is expected excellent properties, but there are a lot of difficulties due to highly crystalline structure.

Reaction scheme of our recent work



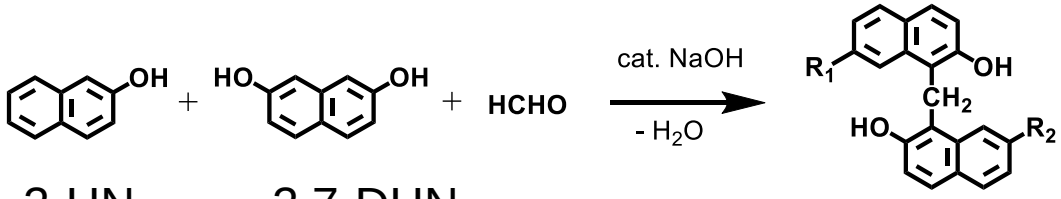
Difficult handling, solid state (high melt viscosity)



Difficult handling, strong crystallinity (melting point is more than 200C, beyond the curing temperature)

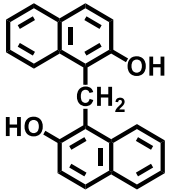
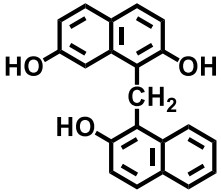
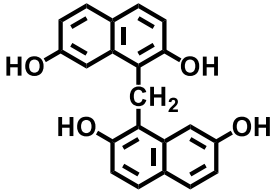
This work

To suppress the crystallinity by combination of naphthalene unit monomer.

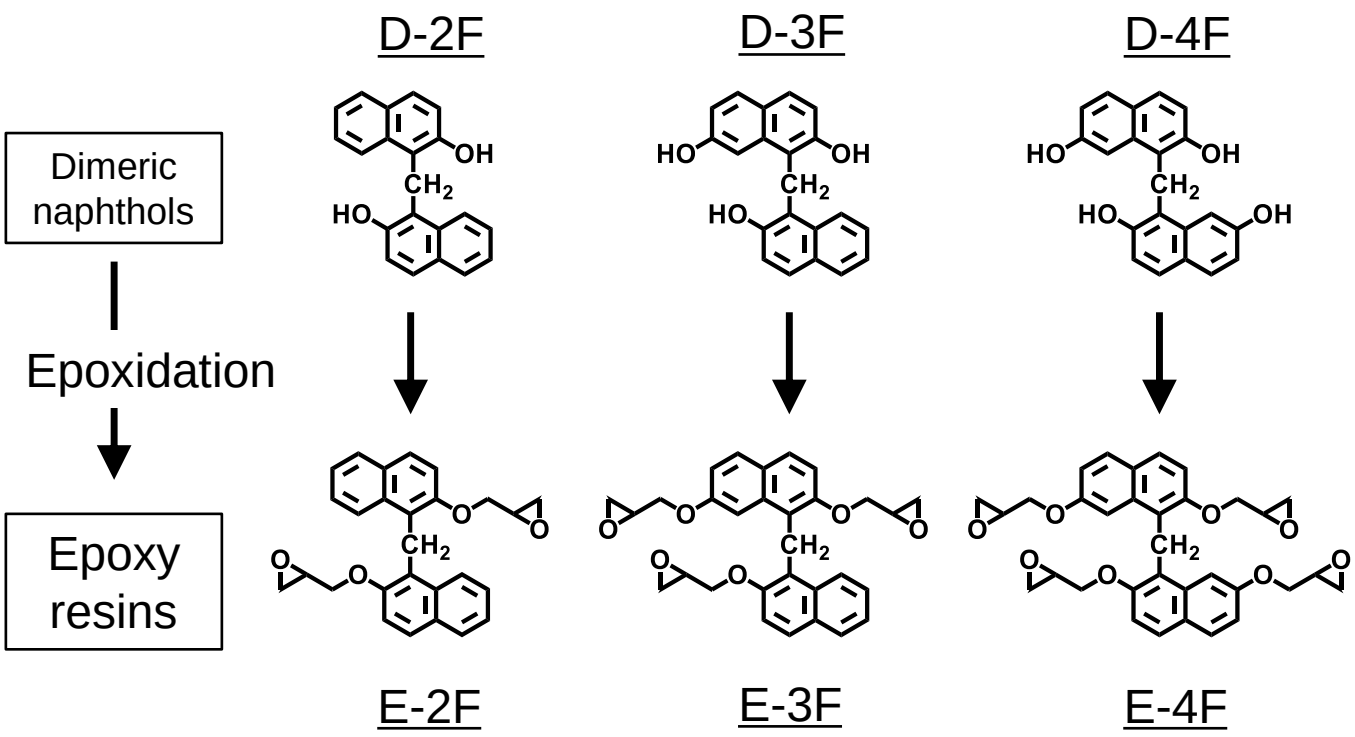


2-HN 2,7-DHN

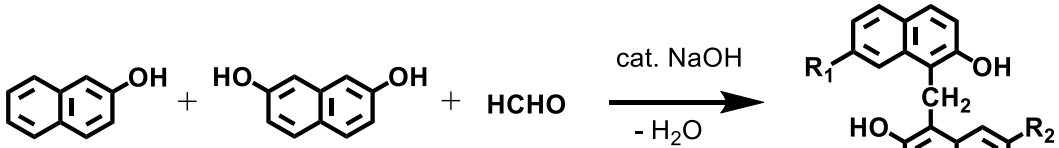
R_1 : H or OH
R_2 : H or OH

	D-2F	D-3F	D-4F
R_1	-H	-OH	-OH
R_2	-H	-H	-OH
Chemical structure			

Epoxidation of the dimeric naphthols



Synthesis results of this work



2-HN 2,7-DHN

R_1 : H or OH
R_2 : H or OH

Run	Starting materials (mol ratio (%))			Reaction products				
				Product code	Dimeric naphthols (mol ratio (%))			Total hydroxy functionalities (number / molecule)
	2-HN	2,7-DHN	F		D-2F	D-3F	D-4F	
1	0	100	50	DN-a	0	0	98.5	4.0
2	50	50	50	DN-b	25.5	52.6	18.4	3.0
3	70	30	50	DN-c	50.1	36.9	9.3	2.6

Epoxy resin properties

Run	**Dimeric Naphthols**	**Epoxy resins**			
	Product code	Product code	E.E.W (g/eq)	Softening point (°C)	Melt viscosity (150°C, mPa.s)
4	DN-a	E-a	165	91	450
5	DN-b	E-b	189	79	250
6	DN-c	E-c	205	72	70
Control		E-BPA	188	liquid	15
		E-PN	181	semi-solid	34

Evaluation method

Evaluation procedure (neat resin)

Mix

Epoxy resin and curing agent (4,4'-DDS) was weighted at stoichiometric ratio.

↓

Degas

The mixture was homogenized and degassed in vacuum. If necessary, the mixture was heated around 80 to 100℃.

↓

Casting mold

The degassed mixture was casted in the mold.

↓

Cure

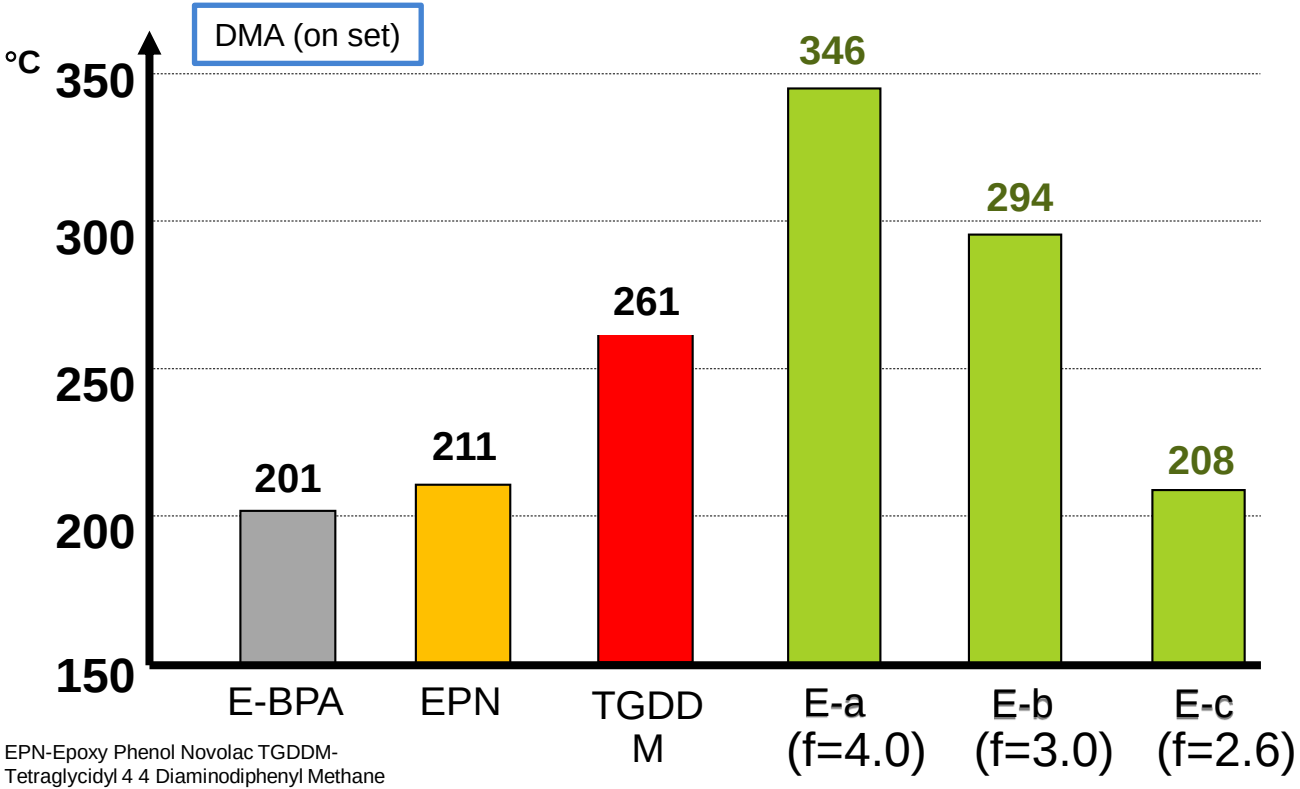
The mixture in the mold was cured by oven. Curing condition was 150℃/1hr + 180℃/3hr.

↓

Cutting

The cured resin was cut to the sample size for several test (DMA, Flexural test, Tensile test, etc).

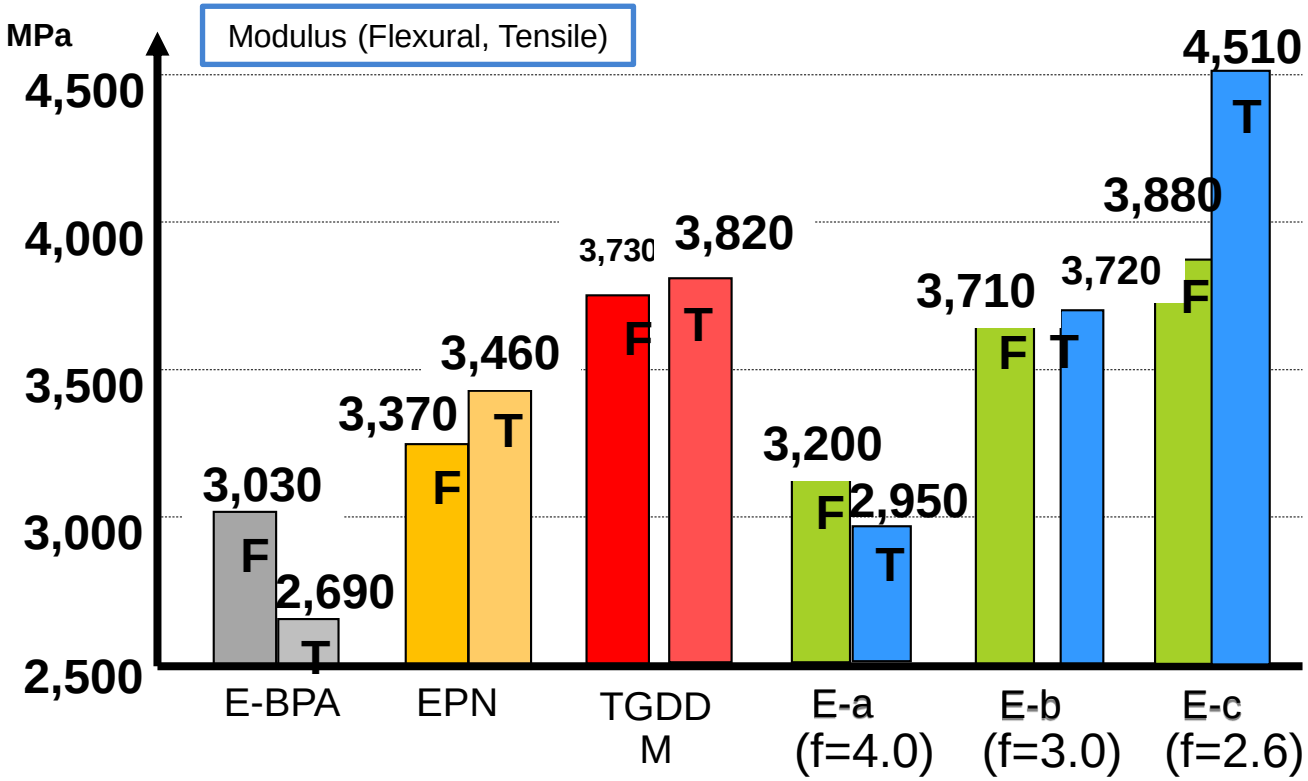
Glass Transition Temperature of Cured Resins



EPN-Epoxy Phenol Novolac TGDDM-Tetraglycidyl 4 4 Diaminodiphenyl Methane

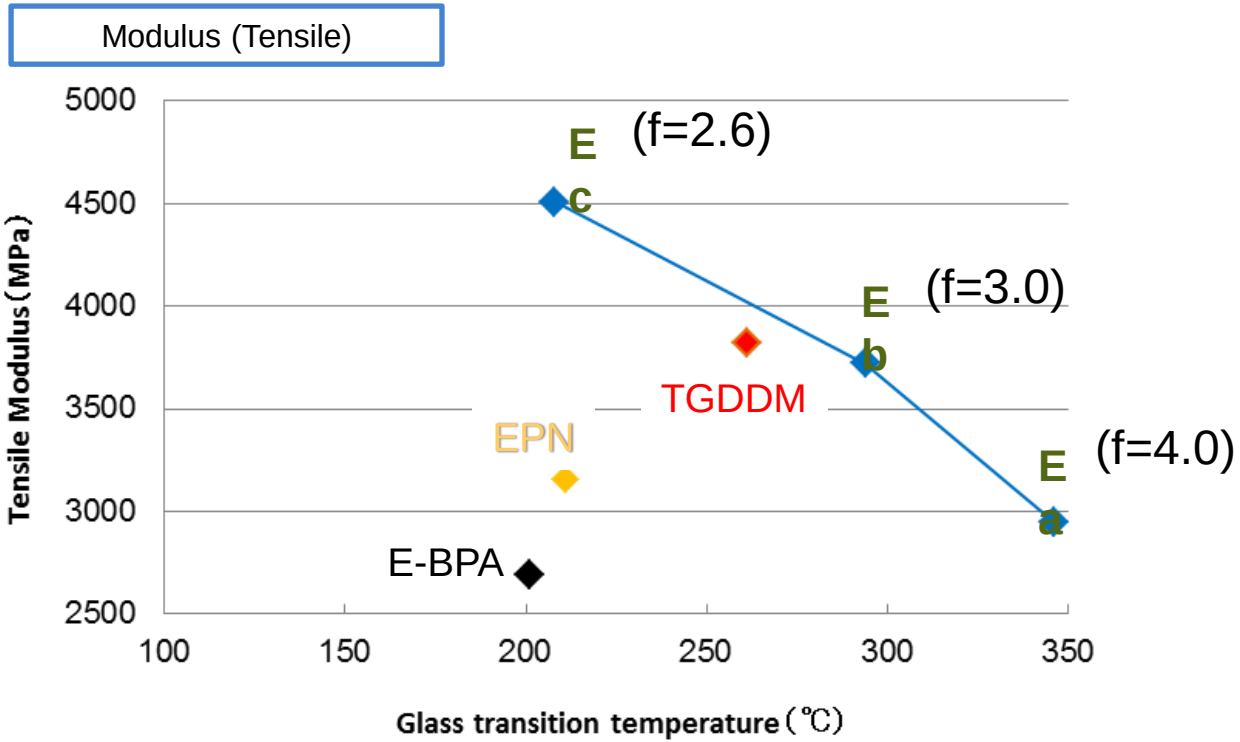
■ Hardener : DDS (4,4'-Diamino-diphenylsulfone), Stoichiometric ratio
■ Cured condition : 150°C×1hr + 180°C×3hr

Modulus of Cured Resins



■ Hardener : DDS (4,4'-Diamino-diphenylsulfone), Stoichiometric ratio
■ Cured condition : 150°C×1hr + 180°C×3hr

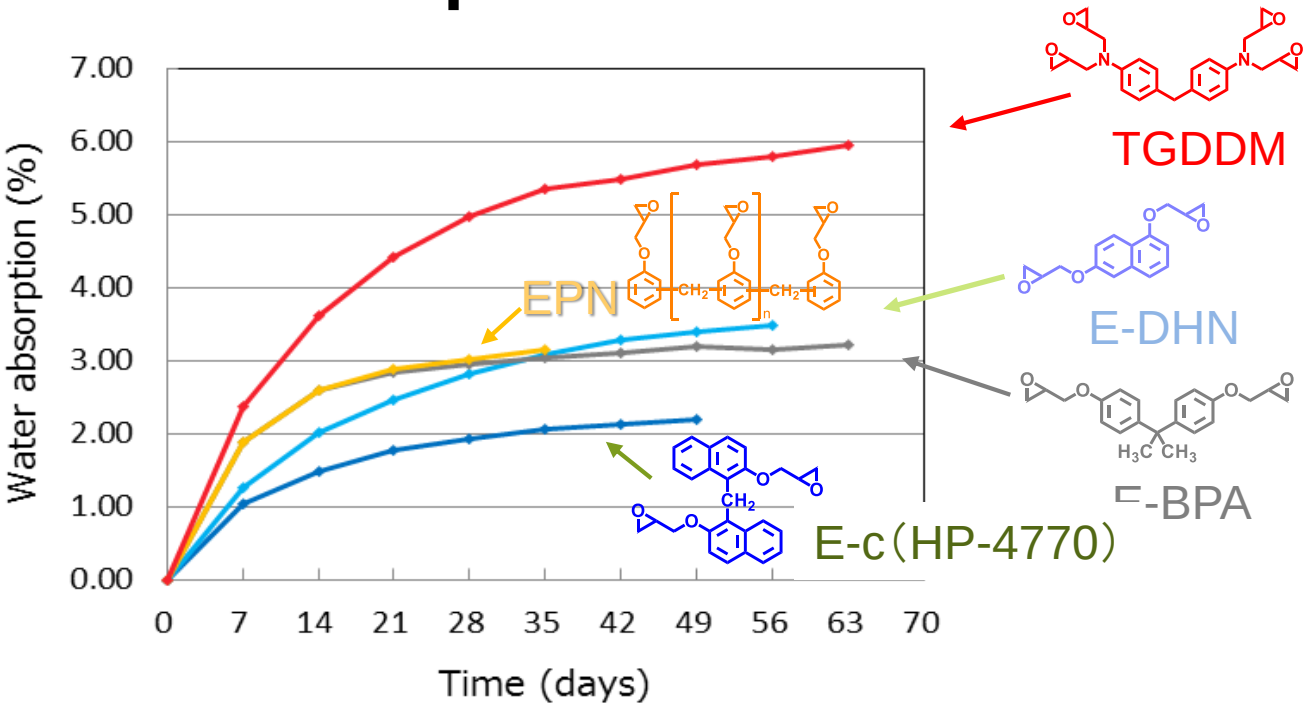
Relationship between Tg and Modulus of Cured Resins



Ea provide excellent high Tg, and **Eb** & **Ec** provide high modulus to their cured resin.

- Hardener : DDS (4,4'-Diamino-diphenylsulfone), Stoichiometric ratio
- Cured condition : 150°C×1hr + 180°C×3hr

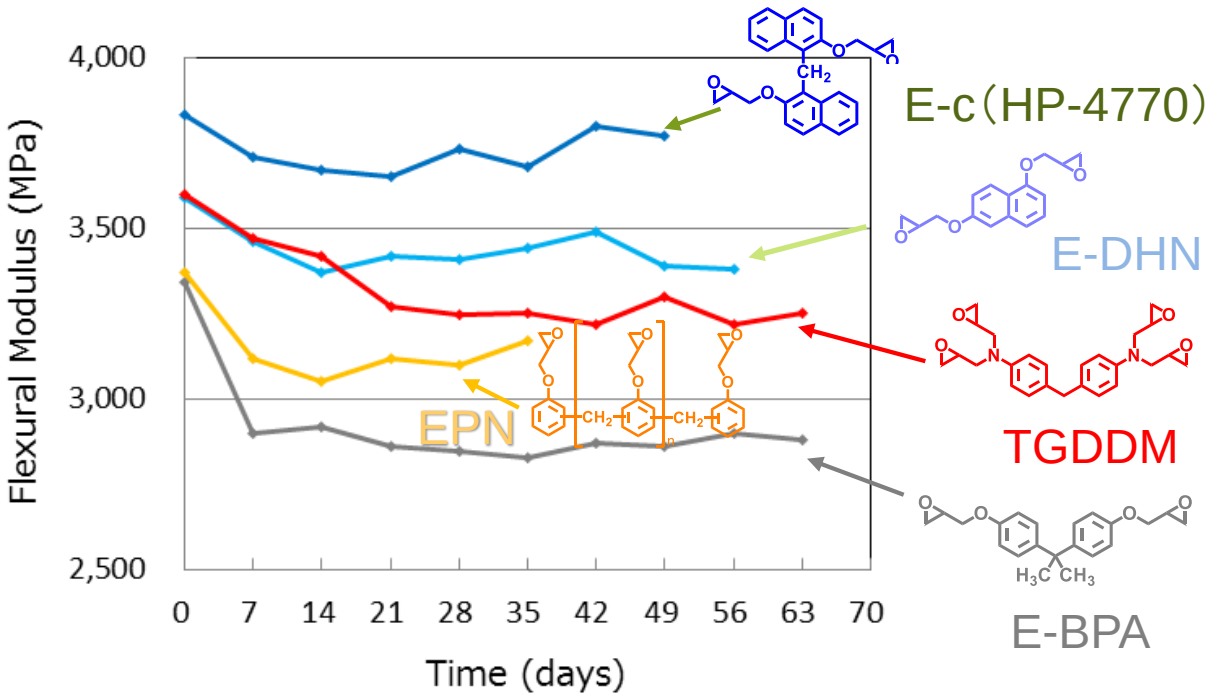
Moisture Absorption of Cured Resins



Ec provide the cured resin with low moisture absorption, about 2/3 that of E-BPA, about 1/3 that of TGDDM.

- Hardener : DDS (4,4'-Diamino-diphenylsulfone), Stoichiometric ratio
- Cured condition : 150°C×1hr + 180°C×3hr
- Test condition : Dipping cured samples in Hot water (70°C)

Hot-Wet properties (Flexural Modulus changes after wet condition)



Ec provide excellent Hot-Wet properties to its cured resin.

- Hardener : DDS (4,4'-Diamino-diphenylsulfone), Stoichiometric ratio
- Cured condition : 150°C×1hr + 180°C×3hr
- Test condition : Dipping cured samples in Hot water (70°C)

Processes & Applications

CFRP's (carbon fiber reinforced plastic) compressive strength

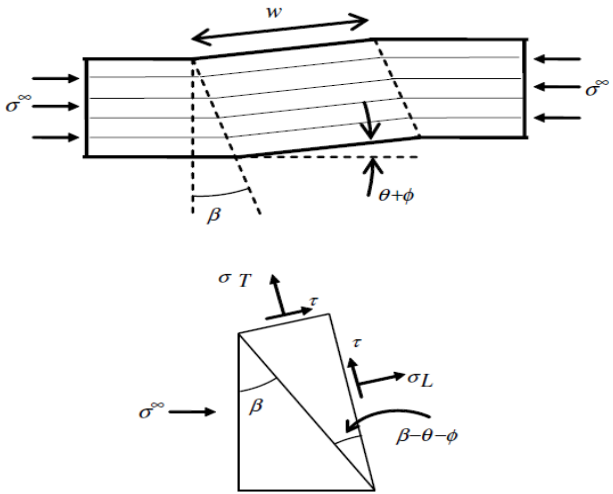


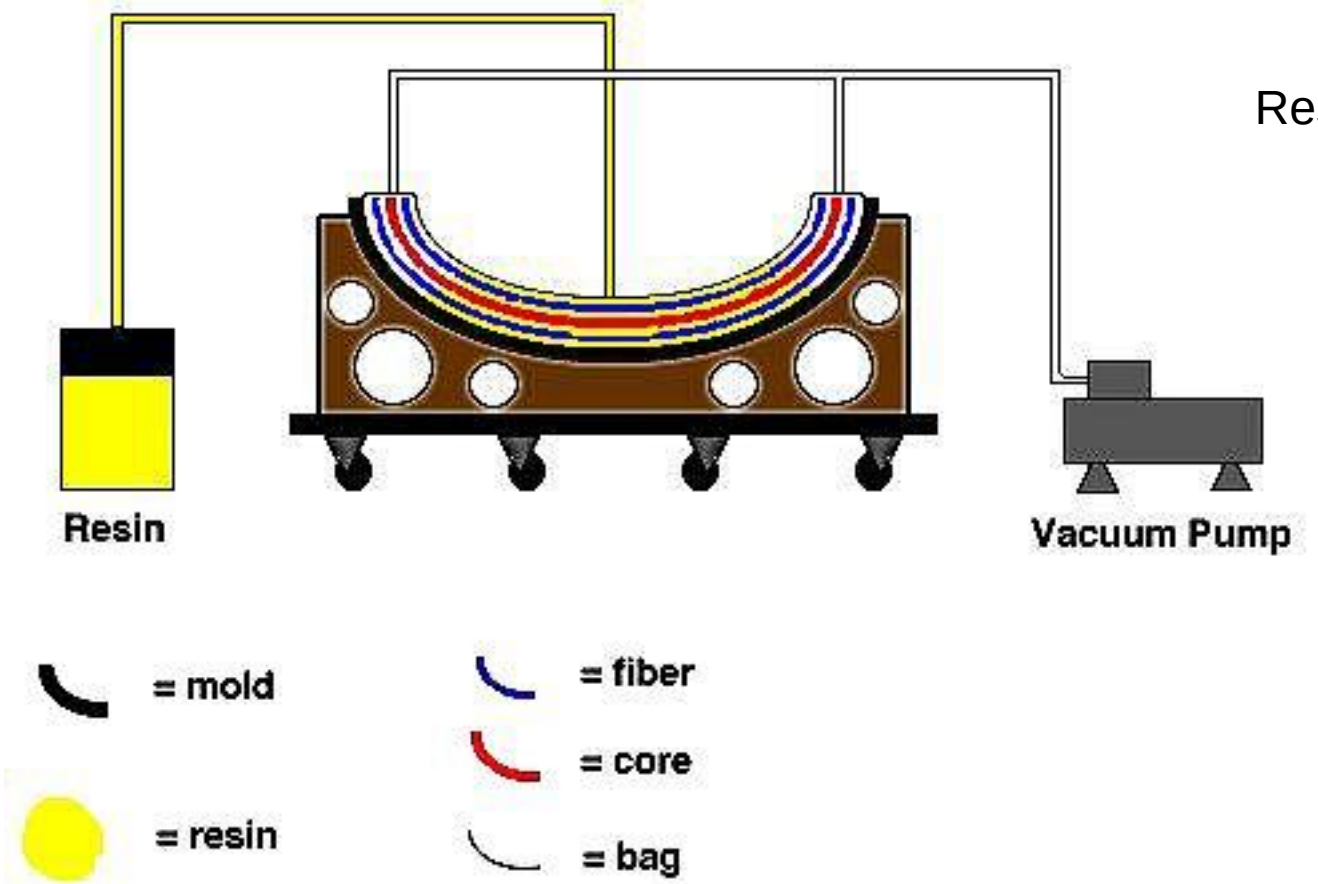
Fig. 1. Kink band model.

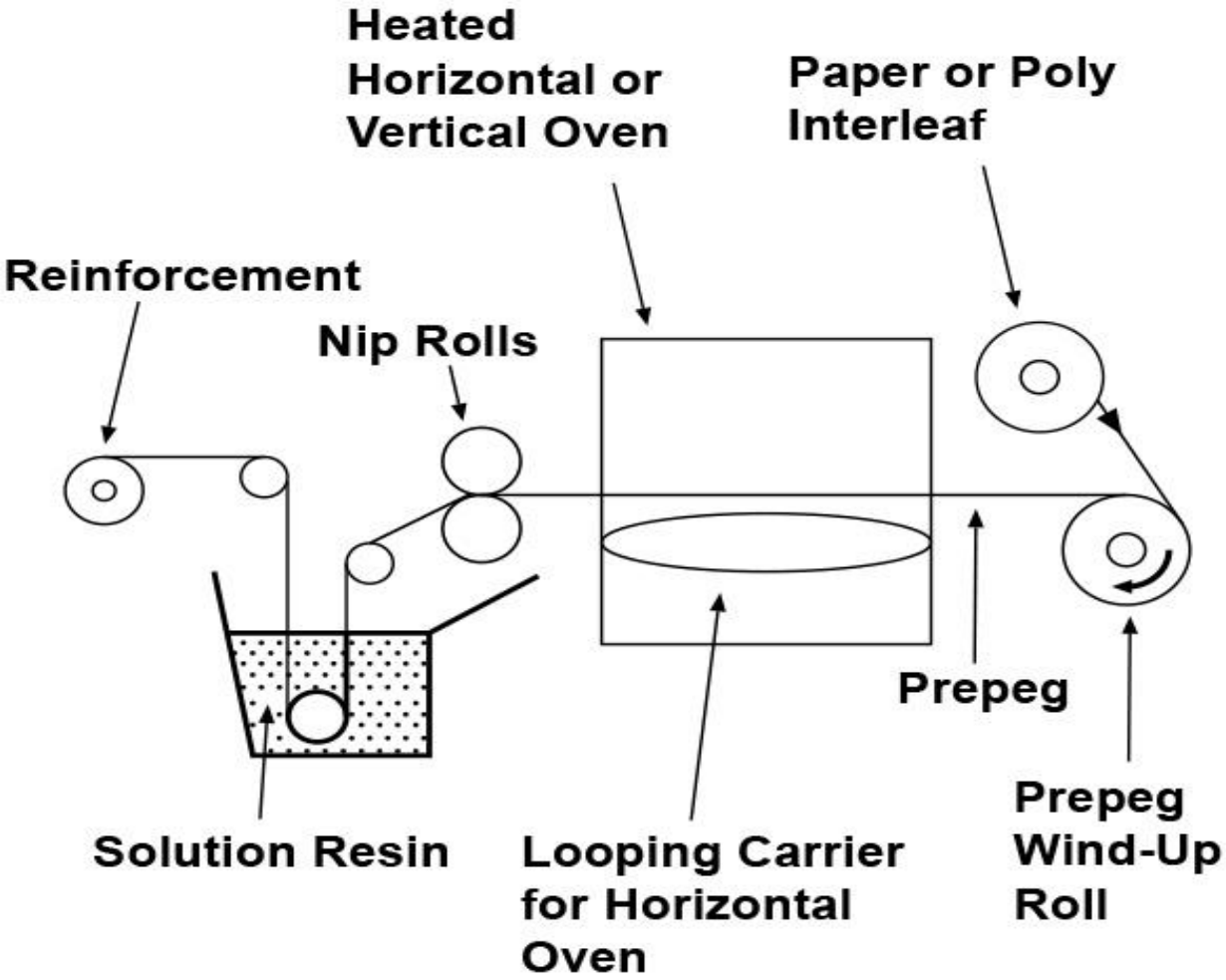
Why it matters?

CFRP's compressive strength greatly depends on the shear rigidity of the resin, and it is theoretically and experimentally confirmed that <u>the high modulus resin is effective</u>.

T. Yokozeki, T. Ogasawara, T. Ishikawa : Composites Science and Technology, 65, 2140 (2005)

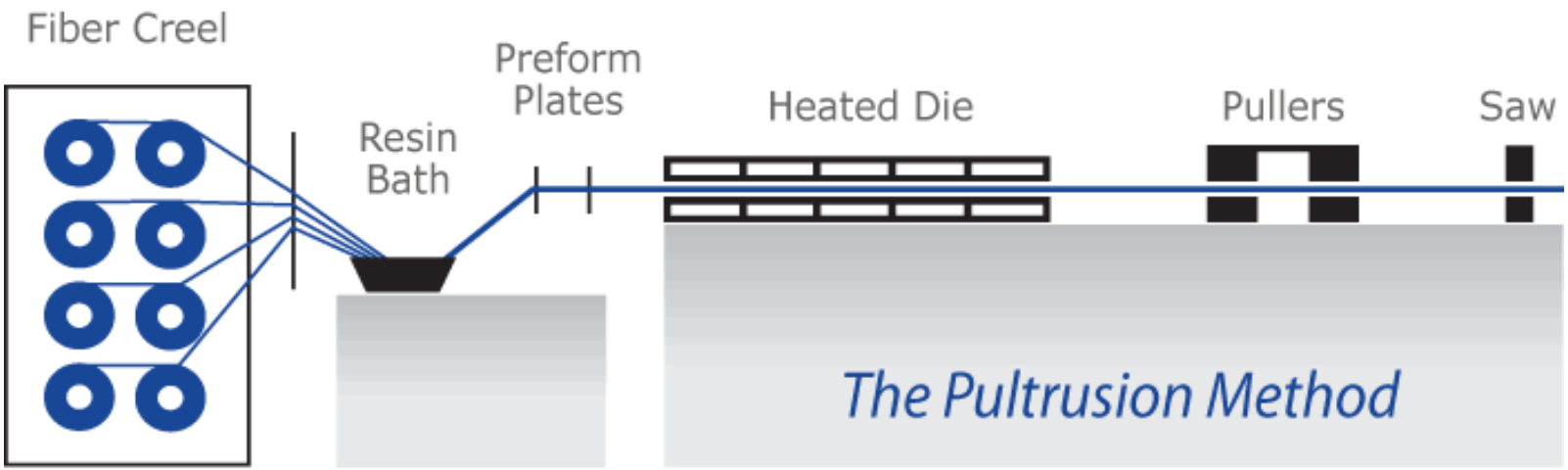
Resin Infusion



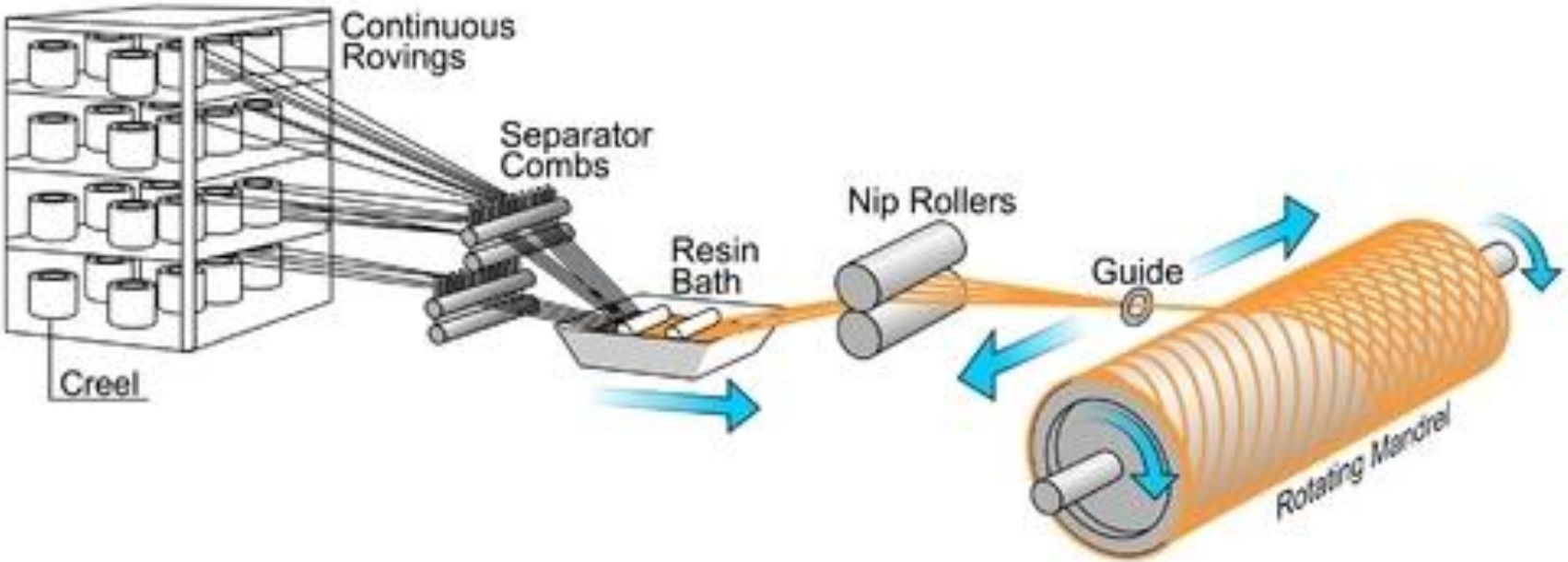


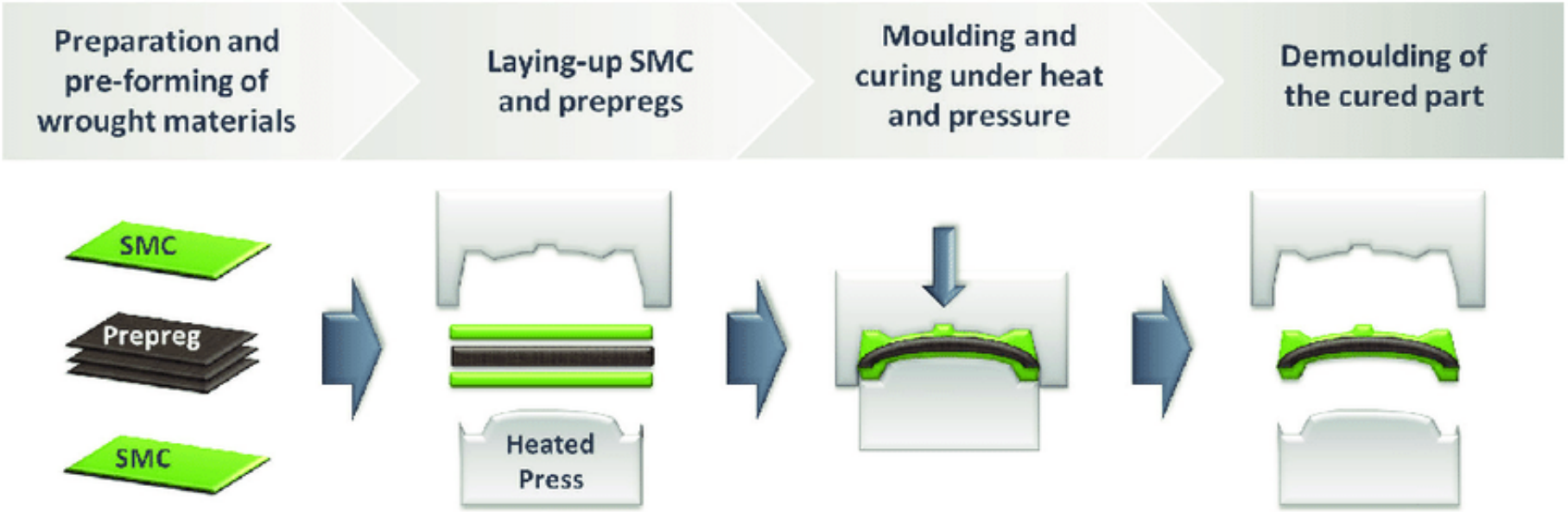
B Stage Prepreg

To the Freezer

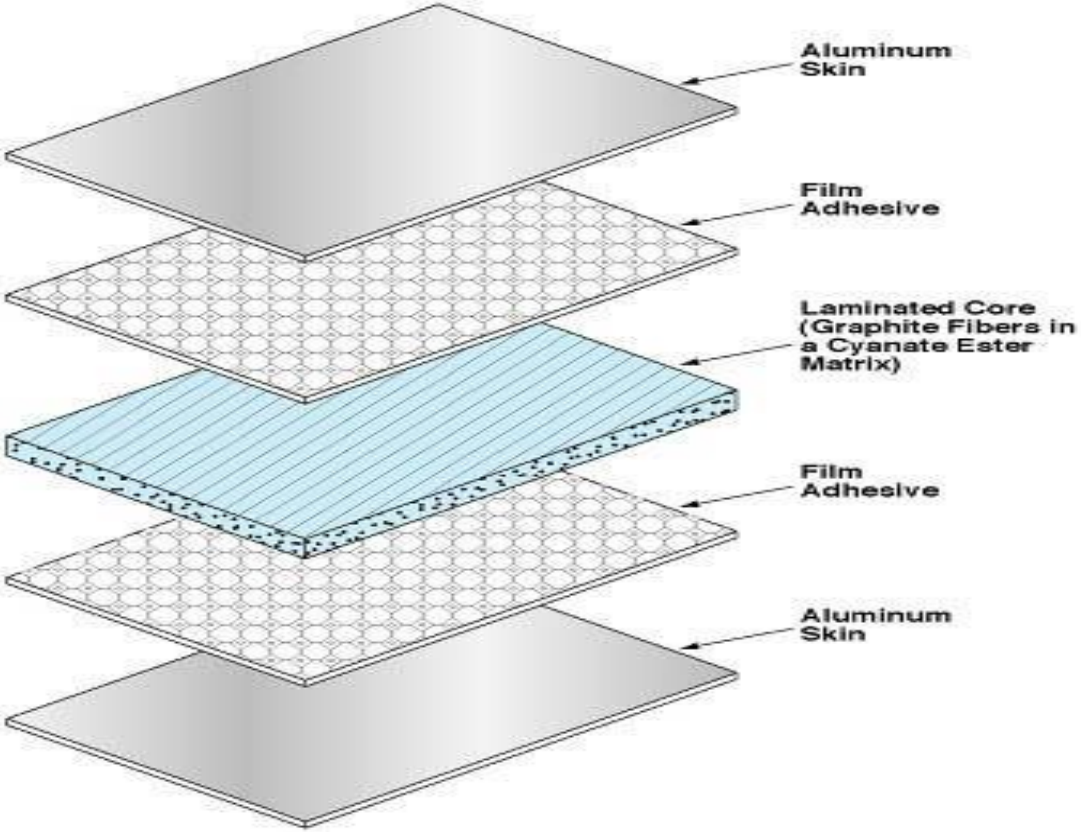

Fiber Creel
Resin Bath
Preform Plates
Heated Die
Pullers
Saw
The Pultrusion Method

Filament Winding




Preparation and pre-forming of wrought materials
Laying-up SMC and prepregs
Moulding and curing under heat and pressure
Demoulding of the cured part
SMC
Prepreg
SMC
Heated Press

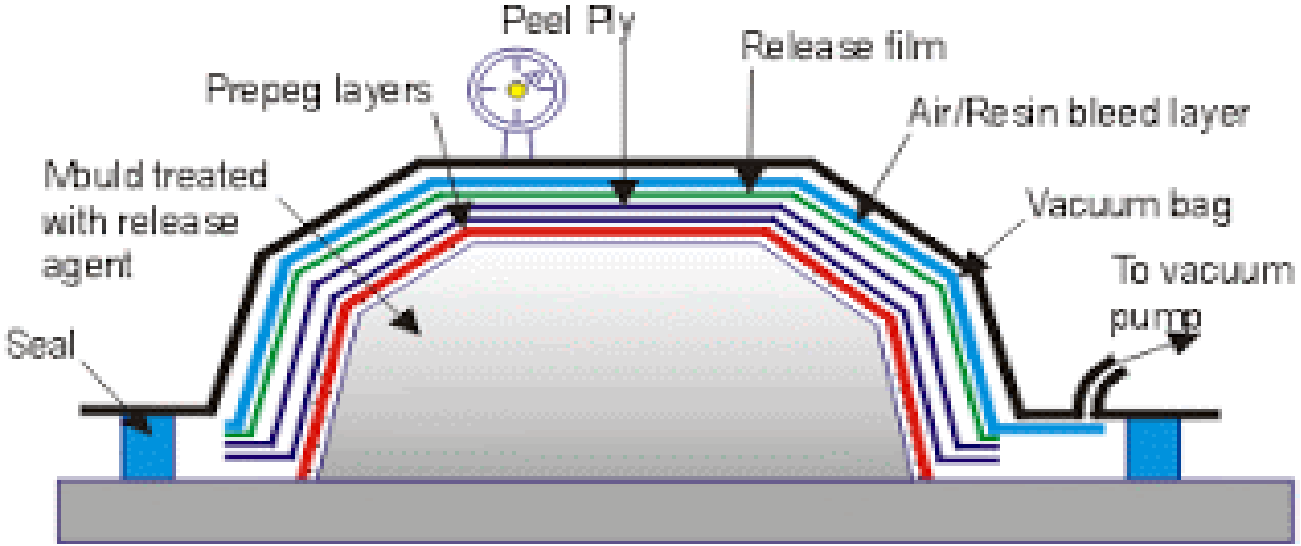
Film Adhesive



Heat Sink for PCB (printed circuit board)

Film & Direct Impregnation

Vacuum Bagging-Autoclave Cure



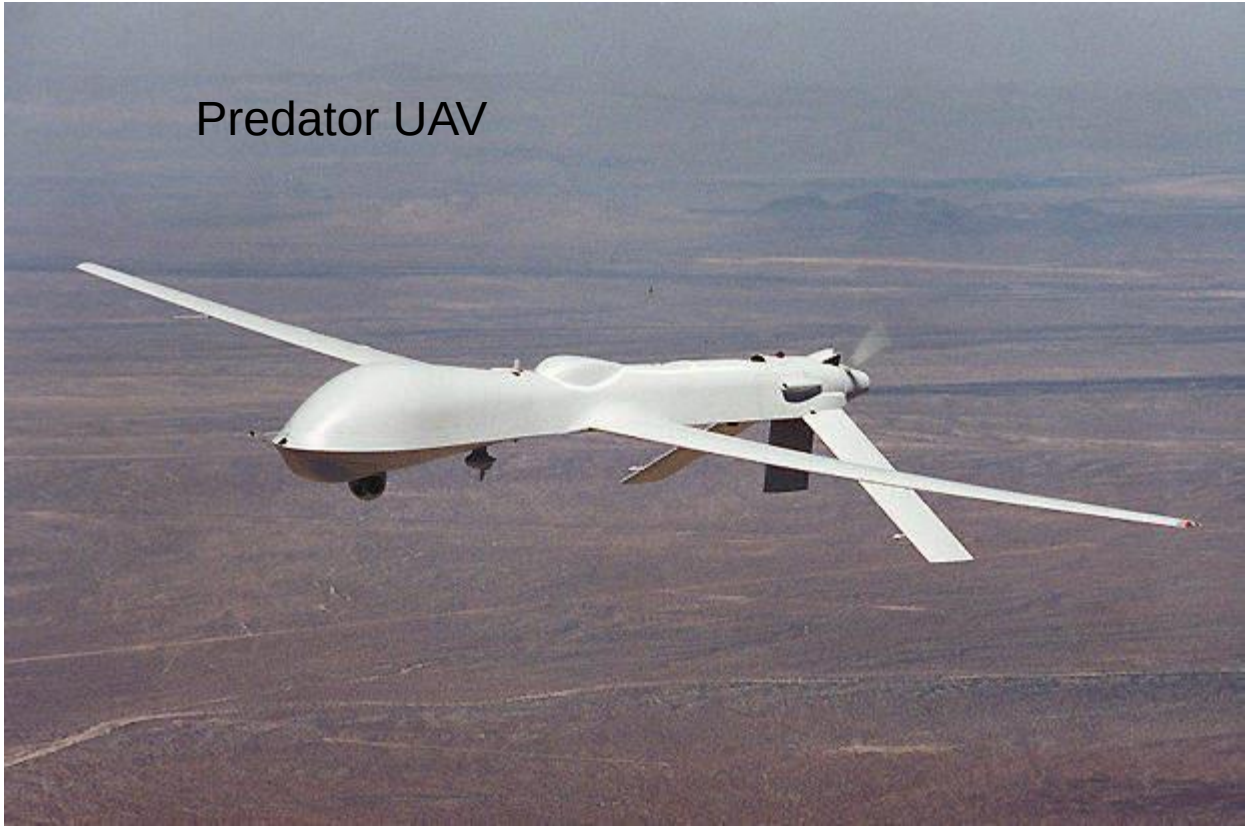
The chassis of the BMW 7-series combines steel, aluminum, and carbon-fiber-reinforced plastic. In the image above, the black parts around the door frames and across the roof are carbon fiber.

B-2 Bomber Aerostructure

Hot/Wet; High Modulus;Low Moisture

Fracking Plug

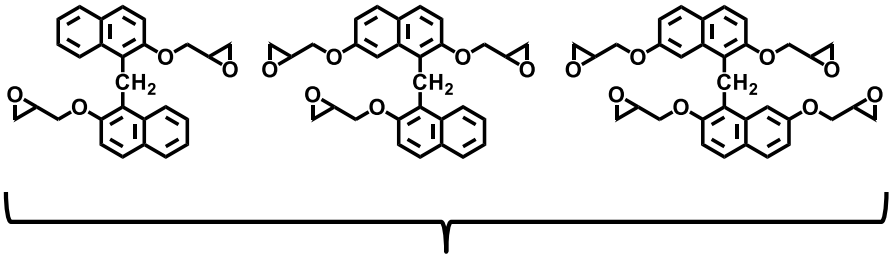

PAC-3


Predator UAV

Conclusion

- We synthesized the new multi-functional epoxy resins containing Naphthalene unit.
- Cured resins exhibited high Tg, high modulus and excellent hot-wet properties suitable for composite and electronic applications.

The new epoxy resins



Combination with these chemical structures

Thank You!

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- **Bio: 30+ years in the materials & processing arena for aerospace, defense, electronics and transportation industries.**