BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS
FACULTY OF MECHANICAL ENGINEERING
DEPARTMENT OF POLYMER ENGINEERING

DEVELOPMENT OF STRUCTURAL FIBER REINFORCED POLYMER COMPOSITES FOR AERONAUTICAL APPLICATIONS

Theses booklet

WRITTEN BY: Péter Niedermann
MSc in Mechanical Engineering

SUPERVISOR: Andrea Toldy, PhD
Assistant Professor

2015, Budapest

- 2 -

The referees' opinion and the minutes of the PhD examination can be viewed at the

Dean's Office of the Faculty of Mechanical Engineering at Budapest University of

Technology and Economics

1. INTRODUCTION

Nowadays the significance of polymer composites with thermoset matrices is growing in the field of "high-tech" industry. The typical application fields are the automotive and aeronautical industries and wind turbine blade manufacturing. The first two sectors represent 50% of the total composite manufacturing worldwide. In these areas the primary aim is to improve the mechanical properties coupled with weight decrease. In the past years several solutions were worked out to achieve this goal, mainly from fossil, petrol based components. Consumer demand for all petroleum based products as well as for oil continues to grow, which predicts the depletion of oil stocks.   In the aeronautical industry the typical thermoset matrix is epoxy resin and mainly carbon fiber is used as reinforcement. To fulfill the strict aeronautical manufacturing requirements, reproducible high quality has to be achieved with low failure rate and low cycle times. This aim can be achieved more easily with constant quality components synthesized under laboratory circumstances.

Due to the depleting mineral oil stock the investigation of replacing synthetic polymer composite components by other alternative sources became necessary. One of these alternatives is to use renewable natural sources. Many investigations dealt with the production of renewable matrices and fiber reinforcements. As the natural sourced components can decrease the composite properties, the mixing of the synthetic, petrol based and renewable components to achieve proper quality is widely investigated.

Another important aspect is the recyclability and the environmental load of the thermoset polymer composites at the end of their lifetimes. Because of the origin and structural build-up of renewable sourced thermoset composites, these materials are potentially biodegradable. This form of waste processing provides a feasible alternative besides the currently not yet abundantly used material recycling.

The aim of this work is to develop partially or entirely renewable sourced fiber reinforced thermoset polymer composites and to investigate their application possibilities as aircraft structural materials.

2. SUMMARY OF THE LITERATURE, OBJECTIVES OF THE DISSERTATION

According to the literature, due to the depleting stock of mineral oil and increasing environmental awareness the development and characterization of natural based composite components is a highly investigated area. Some research works dealt with mixture of the synthetic and renewable sourced components, but there are some investigations developing and characterizing fully bio-based composites as well. Nowadays the "high-tech" composite industry also searches for renewable sourced alternatives to replace the currently easily accessible petrol based components, for example in the field of automotive and aeronautical industry. The versatility of nature provides many solutions to reach this goal.

The currently most applied base epoxy component in composite industry is the petrol based aromatic DGEBA. According to the literature there are several methods to replace this component with bio-based epoxy components. Natural epoxy resins can be prepared from plant oils (soybean or linseed oil) and from polysaccharide (sorbitol or cardanol) as well. Epoxy components require curing agents to form the three dimensional crosslinked structure of the matrix material. These curing agents can be synthesized also from natural sources (polysaccharides and carbonic acids). The mechanical properties of these matrices do not reach that of DGEBA yet, but with proper fiber reinforcement, in the future they could replace the petrol based systems in composite systems.

Instead of the commercial glass or carbon fiber, jute fiber can be used as composite reinforcing material, if it fulfills the requirements for mechanical properties. The availability of jute is much higher than in case of commercial hemp or flax, and its worldwide production is much higher as well. The advantage of the natural sourced plant fibers, that no expensive technologies are necessary to create the fiber form because it is naturally provided. However, the fluctuation of the composition, and therefore the mechanical properties represents a disadvantage, consequently, its application in structural composites is not yet solved.

The applicability of jute fibers in composite industry is a widely investigated area. One of the most important properties in polymer composites is the adhesion between the fiber and the matrix material. According to the literature in the field of the improving the adhesion properties there are many positive and negative results as well. Ultimately with alkali (NaOH solution) treatment it was possible to eliminate the environmental effects of the fibers and to improve the adhesion between the fibers and the matrix material.

The main advantage of the fully bio composites compared to the partially or entirely synthetic ones, that the matrix and also the reinforcing material is potentially degradable in natural environment, which provides biodegradability without environmental damage.

According to the literature no research was carried out to study the mixing of aliphatic, potentially natural sourced, but currently petrol based resins and epoxidized soybean. Also their application as polymer composites was not yet investigated. Glucose based epoxy components and their application as polymer composite matrix material was also not yet described in the literature. The investigation of these two material groups is very important either with natural sourced plant fiber reinforcement (jute) for indoor applications or with petrol based fibers (carbon fiber) as structural materials.

Based on the literature overview my objectives were the following:
- partially or fully replacement the synthetic, petrol based epoxy components with renewable sourced systems,
- development and investigation of partially or fully natural based matrices for technical applications,
- reinforcement of these systems with natural based plant fibers,
- mechanical characterization of the developed fully or partially bio-based, natural fiber reinforced composite materials,
- development of carbon fiber reinforced renewable based epoxy matrix composites for structural applications,
- development of composite sandwich structure with plant fiber reinforcement and renewable sourced matrix for aeronautical applications.

3. MATERIALS AND METHODS

3.1. MATERIALS

In case of the material selection the requirements set by Dassault Aviation, industrial partner in the related European research project, were taken into account. The most critical parameter was the proper T_g of the matrices (>120°C and >180°C). After pre-examinations, the materials, processes and test methods were chosen in agreement with the industrial partner.

Matrices

The developed and examined matrices had to be fit to the following properties:

1. $T_g > 120°C$, processable with prepreg technology, and applicable with natural fibre reinforcement for sandwich composite structures for interior aircraft applications.

2. $T_g > 180°C$, processable with prepreg, Liquid Resin Infusion and Resin Transfer Moulding technology to produce carbon fiber reinforced composites for structural aircraft applications.

Epoxy components

Table 1 shows the used commercial and synthesized (by the Budapest University of Technology and Economics, Department of Organics Chemistry and Technology) epoxy components during my research work.

Epoxy component	Main component	Manufacturer	Trade name	Viscosity (Pas; on 25°C)	Epoxy equivalent (g/eq)
ESO	epoxidized soybean oil	Emery Oleochemicals Ltd.	Edenol D81	0.53	246
GER	triglycidyl ether of glycerol	IPOX Chemicals Ltd.	MR3012	0.15	144
PER	triglycidyl ether of pentaerythritol	IPOX Chemicals Ltd.	MR3016	1.05	168
DGEBA	diglycidyl ether of bisphenol-A	IPOX Chemicals Ltd.	ER1010	1.95	188
GFTE	triglycidy ether of glucofuranoside	BME Department of Organic Chemistry and Technology	-	3.77	160
GPTE	triglycidy ether of glucopyranoside	BME Department of Organic Chemistry and Technology	-	solid at room temperature	160

Table 1 Epoxy components and their main properties

Curing agents, catalysts

As curing agents of the epoxy components commercial amine and anhydride type curing agents were used, which are also preferred in the aerospace industry. Table 2 shows the applied curing agents and the catalyst used in case of anhydride type crosslinking agent. The mixing ratio of the epoxy/curing agent was determined in every case on the basis of stoichiometric principals, using the epoxy equivalent (*EEW*), anhydride (*AEW*) and amine hydrogen equivalent (*AHEW*) values. The *EEW* value means the epoxy component mass in grams, which contains 1 mol epoxide function. The AEW and AHEW value means the mass

of the curing agent, which contains 1 mol anhydride group or 1 mol active hydrogen bonded to nitrogen (-NH).

Curing agent	Main component	Manufacturer	Trade name	Viscosity (mPas; on 25°C)	Amine/anhydride equivalent (g/eq)
AR917	methyl-tetrahydrophtalic-anhydride	Huntsman Advanced Materials	Aradur 917	75	160
DY070 (catalyst)	1- methylimidazole	Huntsman Advanced Materials	DY070	≥ 50	-
DETDA	diethyl-toluene-diamine	Lonza Ltd.	DETDA80	150	45

Table 2 Curing agents and the catalyst and their main properties

Table 3 shows the mixing ratios of the epoxy/curing agents. In case of the anhydride type curing agent, 2 mass% catalyst, related to the mass of the epoxy resin, was added to the mixture.

Epoxy component	ESO		GER		PER		DGEBA		GFTE		GPTE	
Curing agent	AR917	DETDA	AR917	DETDA	AR917	DETDA	AR917	DETDA	AR917	DETDA	AR917	DETDA
Mass ratio	100:65	-	100:105	100:31	100:96	100:27	100:90	100:25	100:100	100:28	100:100	100:28

Table 3 Applied mixing ratios

To investigate the effect of the alkali treatment, distilled water and >97% purity NaOH pellets (provided by Sigma Aldrich) were used.

For sandwich composite structure preparation 6.5 and 20 mm thick Rohacell XT110 type open-cell polymethacrylimide foams with 110 kg/m^3 density were used.

Reinforcements

Jute fabric

For composite preparation untreated, woven, rough jute fabric was used with 270 g/m^2 areal weight (provided by Műszaki Konfekció Kft.). In weft and chain direction, the yarns have the same elemental fibre content, which was determined by calculating the yarns' linear density. The fabric contained 0.6 yarns/mm in weft and 0.5 yarns/mm in chain direction.

Carbon fabric

The applicability of sugar based epoxy resins as structural composites was studied with petrol based, synthetic carbon fabric. MX CST 200 type woven fabric treated for epoxy resin matrices with 200 g/m^2 areal weight (provided by SGL Technologies GmbH) was used. The reason for choosing this reinforcing material was the minimal deviation in mechanical properties compared to jute fabric. In this case the roving content in weft and chain direction was identical (0.5 rovings/mm) and the fibre content of the rovings was the same as well.

3.2. PROCESSING METHODS

Resin specimens

For resin specimen preparation resin moulding technique was worked out. Two and four mm thick spacing element was placed between two steel plates and fixed on three points to avoid resin leaking during the heat treatment.

Composite preparation

Before composite and sandwich composite structure preparation a drying procedure was carried out on the jute fabric at 80°C under 50 mbar vacuum in a vacuum oven (1465_VAC, Sheldon Manufacturing Inc.) in order to eliminate the water content.

The jute and carbon fiber reinforced composites were prepared by pressing technique with pressing plates. In case of the jute fabric six, while in the case of carbon fabric eight layers were used. The composite laminates were made by hand lamination in a press mould and then these laminates were put under compression with 200 bar hydraulic pressure in a Collin Teach-Line Platen Press 200E (Dr. Collin GmbH, Munich, Germany). The heat treatment of the laminates (same as in case of matrices) was carried out during the pressing.

Sandwich composite structures with 6.5 and 20 mm thick core were prepared from sugar based and DGEBA epoxy components cured with anhydride type curing agent. The reason for choosing this core material was its high thermal stability (up to 240°C). The heat treatment parameters were identical to those applied during composite preparation.

3.3. TEST METHODS

In case of the fiber content determination, strip tensile tests, tensile, bending and Charpy-tests the measurements were carried out on 23±1°C and with 59±3% relative humidity.

Fiber content determination

The pressed composite laminates' fiber content was determined by the formula (1) below:

$$\Psi = \frac{n_{layer} \cdot A_{comp} \cdot \Psi\prime}{m_{comp}}, \tag{1}$$

Ψ – fiber content of the composite [mass%], n_{layer} – number of layers [pieces], A_{comp} – area of the composite [m²], $\Psi\prime$ – areal weight of the reinforcement [g/m²], m_{comp} – mass of the composite [g].

In case of jute 61±2, in case of carbon fiber 60±1 mass% fiber content was determined. In case of the jute before the fiber content determination, a drying procedure was applied at 80°C for 2 hours to eliminate the water content. In composites, these fiber content values were proper enough, according to the literature.

Strip tensile tests

Strip tensile tests were carried out on the jute fabric according to EN ISO 13934-1:2000 in weft and chain direction with a Zwick Z020 universal tensile tester used a 20 kN force cell. Strip tensile tests were used to study the effect of the alkali treatment also. During the tests the force – crosshead displacement data were recorded. Based on the recorded data specific yarn tensile force values of the strips were determined. 5 specimens were used in every case.

DSC tests (Differential Scanning Calorimetry)

To investigate the curability of epoxy resins and the curing processes with different curing agents, DSC measurements were carried out with a TA Instruments Q2000 DSC device, firstly with heat/cool/heat procedure in nitrogen atmosphere. During the temperature ramping specific heat flow, temperature and time values were recorded. After that the specific reaction enthalpy was be calculated by integrating the area below the heat flow – time curve. Based on the second temperature ramp curve, the glass transition (T_g) temperature value was be determined from the curve inflexion point according to EN ISO 11357-1:1999. The

absence of postcuring reactions was regarded as indication, that the conversion rate was appropriate.

As second step, heat treatment was worked out at isothermal conditions for the epoxy resin systems for matrix specimen and composite preparation. The samples were put into the DSC device at a specific temperature for a specific time and the specific heat flow was recorded in function of time. Second heating procedure was applied in this case also to check the proper curing. By integrating the heat flow curve in function of the time the specific reaction enthalpy was calculated. According to EN ISO 11357-5:2001 the quotient of these two specific enthalpies gives the conversion of the resins.

TGA tests (Thermal Gravimetric Analysis)

To compare the cured epoxy components' thermogravimetric properties TGA measurements were carried out with a Setaram Labsys type TGA device in nitrogen atmosphere. During the tests the mass lossof the specimens (TG) was recorded in function of temperature.

TG derivative by time was calculated by the TGA devices' software and the decomposition rate was compared in function of temperature. According to the test results the temperature for the 5 and 50 mass% loss were determined. The remaining mass, the maximum decomposition rate and temperature belonging to is was also determined.

Gelling tests

To determine the gel point (time) of the epoxy resin components with all curing agents gelling tests were carried out with a TA Instruments AR2000 type rheometer at 100°C. 25 mm diameter paralell plate, 200 µm gap and 10 rad/s plate angular velocity were applied. During the tests, storage (G' [MPa]) and loss modulus (G'' [MPa]) were recorded in function of time (t [s]). The gel point of the resin is at that time when the G' equals to G''.

DMA tests (Dynamic Mechanical Analysis)

To compare the different epoxy systems' dynamic mechanical properties DMA measurements were carried out on the resin and the composite specimens as well by a TA Instruments DMA Q800 device. During the tests 0.1% relative strain was set and 1 Hz frequency was applied between 0 and 200°C with 3°C/min temperature ramp. The specimens' T_g values were determined from the *tanδ* curves' peaks.

Tensile tests

On the matrix and composite specimens tensile tests were carried out according to EN ISO 527-4:1999 with a Zwick Z020 type universal tensile tester used a 20 kN force cell. During the tests, force and crosshead displacement values were recorded by the devices' software. From the readings tensile strength and tensile modulus were calculated. For the tests 5 specimens were used in every case.

Bending tests

On the matrix, composite and composite sandwich structured specimens bending tests were carried out according to EN ISO 178:2003 with a Zwick Z020 type universal tensile tester used a 20 kN force cell. During the tests, force and crosshead displacement values were recorded by the devices' software. From the readings bending strength and bending modulus were calculated. For the tests 5 specimens were used in every case.

Charpy-tests

On ESO-epoxy matrix specimens Charpy-tests were carried out according to EN ISO 179-1:2000 by a Resil Impactor Junior device. The specimens' Charpy impact strength values were determined. For the tests 10 specimens were used in every case.

Raman spectrometry

In case of ESO-DGEBA epoxy resin systems phase separation was investigated with Raman mapping. Raman spectra were collected using a Horiba Jobin–Yvon LabRAM system coupled with an external 785 nm diode laser source and an Olympus BX-40 optical microscope. Objectives of 100x magnification were used for optical imaging and spectrum acquisition. The distributions were determined using the reference spectra of pure materials with the Classical Least Squares (CLS) algorithm modeling software.

SEM micrograph (Scanning Electron Microscopy)

From the fracture surfaces of the matrices and composites SEM images were taken with JEOL JSM 6380LA type device in 1000x magnification. The specimens were gold spur coated with a Jeol JPC1200 device before the investigations.

4.   THESES

Thesis 1

The addition of epoxidized soybean oil (ESO - with 220-260 g/Eq epoxy equivalent weight) to petrol oil based, aliphatic epoxy resins can significantly improve the glass transition temperature (T_g) of these systems. In case of glycerol based resin (GER) 26°C and in case of the pentaerythritol based resin (PER) 19°C increase can be reached with methyl-tetrahydrophtalic-anhydride curing agent. This phenomenon can be explained by the compressive stress exposed by the aliphatic resin (cured at lower temperature than ESO according to Differential Scanning Calorimetry results) on the not yet cured ESO-phase. The segmental movement of the ESO phase cured under compressive stress starts at higher temperature than in case of pure ESO and aliphatic base resin [1].

Thesis 2

Curing circumstances of two newly synthesized, renewable sourced, glucose based epoxy components (glucofuranoside-triepoxy (GFTE) and plucopyranoside-triepoxy (GPTE)) were determined with methyl-tetrahydrophtalic-anhydride and diethyl-toluene-diamine curing agents. Optimal heat treatment cycle for processing of glucose based epoxy resins (GPTE and GFTE) was elaborated using isothermal differential scanning calorimetry (DSC) [2, 3].

Thesis 3

The glass transition temperature (T_g) of the trifunctional glucose based epoxy resins (GFTE and GPTE) cured with methyl-tetrahydrophtalic-anhydride and diethyl-toluene-diamine curing agents is similar or significantly higher than the commercial that of the DGEBA. The higher T_g can be explained by the higher crosslink density caused by the higher functionality of the glucose based resins. In case of GPTE cured with diethyl-toluene-diamine curing agent the cured systems' T_g was 36°C higher than in case of DGEBA, determined by DMA. The thermal properties of the GFTE and the GPTE are between the aliphatic and the DGEBA epoxy resin systems. The modulus values were similar, the tensile and bending strength values were lower than in case of the synthetic resins. The reason for this is the asymmetric position of the oxirane functions on the sugar based molecules resulting in less possibilities to form secondary bonds after crosslinking [3].

Thesis 4

In case of jute fiber reinforced composites the DGEBA synthetic epoxy resin component can be replaced by the mixture of pentaerythritol based and epoxidized soybean oil (ESO - with 220-260 g/Eq epoxy equivalent weight) based epoxy component in 75:25 mass ratio cured with methyl-tetrahydrophtalic-anhydride curing agent (if the industrial application allows the 35°C lower glass transition temperature). The mechanical properties (tensile and bending strength, tensile and bending modulus) of the composite with this hybrid matrix were similar to that of DGEBA based composites [4, 6].

Thesis 5

The mechanical properties of the carbon fiber reinforced composites prepared from GFTE sugar based epoxy component and methyl-tetrahydrophtalic-anhydride or diethyl-toluene-diamine curing agents were similar to the properties of DGEBA based composites. This can be explained by the proper fiber-matrix adhesion, and significantly higher strength of the fibres than in case of the matrices. With diethyl-toluene-diamine 4% tensile strength, 11% tensile modulus and 14% bending strength and modulus improvement was achieved compared to the DGEBA composite systems [5].

Thesis 6

Using jute fiber reinforcement, methyl-tetrahydrophtalic-anhydride curing agent and polymethacrylimide foam, in sandwich composite structures better bending properties could be achieved in case of sugar based GFTE epoxy resin component than with synthetic petrol based DGEBA epoxy resin component. The higher polarity of GFTE resulted in better impregnation at the phase boundary of the open-cell foam. In case of 6.5 mm foam thickness the GFTE sandwich composites showed 24% bending strength and 7% bending modulus increment compared to the DGEBA sandwich composites [5].

5. LIST OF THE OWN PUBLICATION

Journal articles (English)

[1]   Niedermann P., Szebényi G., Toldy A.: Effect of epoxidized soybean oil on curing, rheological behaviour, mechanical and thermal properties of aromatic and aliphatic epoxy resins. Journal of Polymers and the Environment, **22**, 525-536 (2014). ($IF_{2014}=1,671$)

[2]   Rapi Zs., Bakó P., Keglevich Gy., Szolnoki B., Niedermann P., Toldy A., Bodzay B., Marosi Gy.: Synthesis and characterization of bio-based epoxy resin components derived from D-glucose. European Polymer Journal, **67**, 375-382 (2015). (*IF$_{2014}$=3,005*)

[3]   Niedermann P., Szebényi G., Toldy A.: Novel high glass temperature sugar-based epoxy resins: characterization and comparison to mineral oil-based aliphatic and aromatic resins. Express Polymer Letters, **9**, 85-94 (2015). (*IF$_{2014}$=2,761*)

[4]   Niedermann P., Szebényi G., Toldy A.: Effect of epoxidized soybean oil on mechanical properties of woven jute fabric reinforced aromatic and aliphatic epoxy resin composites. Polymer Composites (2015). *In press.*
(DOI: 10.1002/pc.23650) (*IF$_{2014}$=1,632*)

[5]   Niedermann P., Szebényi G., Toldy A.: Characterization of high glass transition temperature sugar-based epoxy resin composites with jute and carbon fibre reinforcement. Composites Science and Technology, **117**, 62-68 (2015). (*IF$_{2014}$=3,569*)

Journal articles (Hungarian)

[6]   Niedermann P., Toldy A.: Juta erősítés alkáli kezelésének hatása epoxigyanta kompozitok mechanikai tulajdonságaira. Műanyag és Gumi, **51**, 108-111 (2014).

[7]   Romhány G., Niedermann P., Szebényi G.: Szén nanocső/szénszál erősítésű hibrid kompozit rétegközi I. törési módú fárasztóvizsgálata. Műanyag és Gumi, **48**, 436-440 (2011).

Conference papers

[8]   Niedermann P.: The effect of carbon nanotube filling on the interlaminar mechanical properties of carbon fiber reinforced hybrid composites. in 'Gépészet 2010: Proceedings of the Seventh Conference on Mechanical Engineering. Budapest, Magyarország' 897-902 (2010).

[9]   Romhány G., Niedermann P., Szebényi G.: Mechanical properties of MWCNT/fiber reinforced hybrid composites. in 'International Conference on Technical Textiles and Nonwovens. New Delhi, India' 1-8 (2008).

Other publications

[10] Niedermann P., Szebényi G., Toldy A.: Natural fiber reinforced bio-based epoxy resin composites developed for aeronautical applications. in 'Modification, Degradation and Stabilisation of Polymers (MoDeSt). Prague, Czech Republic' (2012).

[11] Szolnoki B., Rapi Zs., Niedermann P., Toldy A., Bakó P., Marosi Gy.: Égésgátolt epoxigyanta prekurzorok szintézise megújuló nyersanyagforrásból. in 'MTA Műanyag és Természetes Polimerek Munkabizottsági Ülés. Budapest, Hungary' (2012).

[12] Szolnoki B., Bodzay B., Rapi Zs., Bakó P., Toldy A., Niedermann P., Marosi Gy.: Flame retardant epoxy resins from renewable sources. 14th European meeting on Fire Retardancy and Protection of Materials (FRPM13). Lille, France' (2013).

[13] Szolnoki B., Budai D., Niedermann P., Konrád P., Rapi Zs., Bakó P., Bodzay B., Toldy A., Marosi Gy.: Flame retardancy and mechanical properties of sugar-based high-tech epoxy resins. in 'International Conference on Bio-Friendly Polymers and Polymer Additives (BPPA). Budapest, Hungary' (2014).

[14] Niedermann P., Toldy A., Szebényi G.: Cukoralapú epoxigyanta kompozitok fejlesztése high-tech ipari alkalmazásokhoz. in 'MTA Szál- és Kompozittechnológiai Tudományos Bizottsági Ülés. Budapest, Hungary' (2014).

[15] Niedermann P., Toldy A.: Mechanical properties of novel glucose based epoxy resin/jute biocomposites. in '2nd International Conference on Bio-based Polymers and Composites (BiPoCo). Visegrád, Hungary' (2014).