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DEVELOPMENT OF CYCLIC BUTYLENE TEREPHTHALATE MATRIX COMPOSITES

to fulfill the requirements of the PhD degree

BUDAPEST

2012

The referees' opinion and the minutes of the PhD examination can be inspected at the Dean's Office of the Faculty of Mechanical Engineering of the Budapest University of Technology and Economics.

1. Introduction

Nowadays electricity-usage is increasing extremely fast due to globalization, and widespreading of household utilities such as air conditioning devices (Table 1). Production possibilities of this energy is given (by water, coal or nuclear power plants) but transmitting this faces problems – remember the northeastern US blackout in August 2003 which was caused by the obsoleting high voltage transmission lines (HVTL) and their sagging.

Year	Electrical energy consumption [TWh]					
	1990	2000	2005	2009	2010	2011
Hungary	35	33	35	37	38	42
European Union	1803	2528	2661	2926	2906	3037
USA	2923	3356	3660	3829	3873	3873
China	580	1014	1630	3428	3438	3503

Table 1. Electrical energy consumption between 1990 and 2011

The transmission technology utilized nowadays that applies only metallic parts has faced its frontiers because only a given amount of electrical energy can be transferred through a cross section unit due to the temperature rise in the wires (the limit is 80°C). Another problem is wire sagging between the poles. This phenomenon is caused by thermal expansion, material structure and mechanics: the wire gets warm and elongate and is capable to deform elastically and as a consequence of this its own weight bends the wire, so it gets closer to the ground. To minimize sag, low pole distances and high poles are utilized. Sagging is to be avoided because a strong electromagnetic field is generated around the wire and if it gets too close to the ground it may cause health problems. According to earlier studies inhabitants living close to HVTLs have problems like leucosis and sleep disorders more likely. A further problem with metallic parts is corrosion due to the presence of water mainly in the inner steel core.

A possible solution for the problems described above is replacing some metal parts with polymeric composite materials. Their main application in HVTLs may be the load-carrying inner core. Suitable composite materials have much higher stiffness-to-weight ratio than steel so sagging would be reduced which results in a reduction in the above mentioned problems.

For high-tech composites nowadays mostly thermosetting materials (generally epoxy resins) are used. Epoxy resins have excellent mechanical properties that make them suitable for being used as the inner core of a HVTL cable but they are problematic to recycle and tend to micro-crack. Moreover, these resins have to be cured which makes production times longer. To solve these problems a new generation of thermoplastic matrices can be utilized, like the *in-*

situ polymerizable cyclic butylene terephthalate (CBT) oligomer system. It is in solid state at room temperature and has water-like melt viscosity (below 0.1 Pas) above its melting point which makes fiber wet-out easy and polymerizes fast among the reinforcing fibers. Since this is a brand new matrix material no industrially applicable processing technology is developed yet. To process CBT new low pressure technologies may be utilized, which consume much less energy than the currently applied thermoplastic processing technologies. Composite materials with this new CBT matrix are capable to replace the conventional steel cores of HVTLs.

Since CBT is a low viscosity thermoplastic semi-finished composite parts, such as sheets or preforms and tapes may easily be processed with this matrix system. Such materials are highly desired by the composite industry, especially for automotive applications.

The aim of this PhD thesis is to develop composites with CBT matrix which possesses appropriate properties to serve as an inner core of a HVTL. It is also desired to develop technologies for processing CBT into a proper composite matrix material.

2. Short overview of the related literature, goals of the thesis

From the overview of the literature it is clearly seen that high voltage industry needs new materials for cable cores. These materials have to have low coefficient of thermal expansion (CTE) and be capable of operating up to 160°C and have to be crimpable since it has to be fixed somehow. After reviewing composite materials it is obvious that carbon fiber reinforced composites are ideal for this purpose with the almost negligible CTE of the fiber and its electrical conductivity. Choosing the appropriate matrix material is more complicated since thermosetting materials are widespread and a lot of experiences are known with regard to their processing. But these materials tend to micro-crack under long-term cycling load to which they are very much subjected between the utility poles their 30-year-long lifespan. Surprisingly, bending was found to be a more crucial load than tension in case of composite cable cores due to the special loads during mounting and application. Tough thermoplastic materials were overviewed and found to be proper for this application with its special loads. Thermoplastics usually have high melt viscosities originated from their long molecular chains. This problem can be overcome by the *in-situ* polymerization of a reactive thermoplastic resin. Finally a reactive polyester, cyclic butylene terephthalate, was chosen with a low melt viscosity of 0.02 Pas at 190-200°C and good outdoor resistivity of the resulting pCBT, which is chemically identical to PBT. The low viscosity makes impregnation fast and easy but CBT is rather sensitive to process conditions. According to the literature CBT can be polymerized into a proper matrix material with appropriate adhesive connection to the reinforcement. Some of the processing parameters are described, but for example a function between degree of crystallinity and cooling speed or one between viscosity and time in the whole processing temperature range have not been set up. Composites were also produced by different methods like hot consolidation, resin transfer molding and a kind of prepreg method. All of them are complicated and no continuous production method was realized. The IHP process is a quasi-continuous method, but capable of producing literally endless sheets and is rather complicated. These composites were mostly reinforced with glass fibers, carbon fiber reinforced ones were hardly studied.

Toughening agents may be useful for CBT to overcome special processing conditions, like quenching. For this purpose the tough polyester, polycaprolactone was chosen on the basis of the literature. The application of this additive has been partially studied, but some questions are still unanswered especially in the field of CBT/PCL matrix composites.

Some nano-scale modifiers were also examined and found to be useful with CBT, but these nano-materials were not successfully applied in fiber-reinforced composites. Graphene was also not tested but this material is believed to be a suitable agent to increase electrical and heat conductivity. Graphene and carbon fiber reinforced hybrid systems are also to-be-developed. Production of profiles with continuous cross section geometries is the simplest by pultrusion. This process was reviewed and found to be applicable for low viscosity reactive thermoplastics. According to this the pultrusion technology can be adapted to CBT which has not been done so far.

According to the above the goals of this PhD thesis are the followings:

1. Development of a pultrusion method, design of a device and description of the process parameters for CBT.
2. Development of a manufacturing method for carbon fiber reinforced composite sheets with CBT matrix that may serve as semi-finished products for the composite industry and investigates the properties of the resulting composites.
3. Increase toughness with polycaprolactone and find an optimal proportion of it for HVTL-like applications.
4. Increase of the heat and electrical conductivity of CBT with graphene nanoplatelets.
5. Increase of the interlaminar shear properties of the composites through adding polycaprolactone or graphene to the matrix.

3. Applied materials and experimental methods

3.1. Applied materials

Matrix material

As matrix material CBT160 powder was used. For all experiments material from the same lot (#000071-25S-01) was used and it was supplied by Cyclics Europe GmbH. (Schwarzheide, Germany). This CBT160 contains 3 mol% catalyst [67] - Fascat 4101 (butylchlorotin dihydroxide) by Arkema Inc. (PA, USA). Before usage the CBT160 powder was dried in an air-circulating oven at 80°C for 8 h in order to remove residual moisture.

Matrix modifiers

As toughening agent, polycaprolactone (CAPA 6505) with an average molecular weight of 50kDa was supplied by Perstorp Holding AB. (SE) and used as received.

Graphene was used to increase electrical and heat conductivity and to improve interlaminar shear properties of the composites. This material was purchased from XG Sciences Inc. (Lansing, MI., USA).

Reinforcing materials

Two different kinds of carbon fibers were used throughout this study. *Unidirectional* carbon fiber fabric – PX35 FBUD0300 – was supplied by ZOLTEK Zrt (Nyergesújfalú, Hungary) and *woven* carbon fiber structure – Sigratex KDL 8003 – was produced by the SGL Group (Wiesbaden, Germany).

3.2. Applied experimental methods

Two types of experimental methods were used: *characterizations* to examine processing properties and ‘*classical*’ *mechanical tests* to analyze the quality of the produced composites. All mechanical tests were performed at room temperature ($25\pm 3^\circ\text{C}$) and at a relative humidity of $40\pm 5\%$.

3.2.1. Characterization methods

Several characterization methods were used, such as thermal analyses and rheology to study processing parameters and understand how the modifiers alter them.

Rheological tests were performed on a plate-plate rheometer (Ares, Rheometric Scientific, NJ, USA), with a plate diameter of 25 mm. ω had a constant value of 40 rad/sec, the frequency was 20 Hz and the gap size was set to 1 mm.

Differential scanning calorimetry tests were performed using a Mettler Toledo DSC821 device. For the differential scanning calorimetry (DSC) tests 6-8 mg samples were used and subjected to a heating-cooling-heating cycle between $20\text{-}270^\circ\text{C}$ with a heating/cooling rate of $10^\circ\text{C}/\text{min}$, if other is not indicated.

Gel permeation chromatography studies: after polymerization of CBT160 to pCBT a small crushed sample of ~30-70 mg was dissolved in a 1 ml mixture of $\text{CH}_2\text{Cl}_2/\text{HFIP}$ (75%/25%) at 70°C . After complete dissolving 3 ml of chloroform and a few microliters of ortho-dichlorobenzene were added to the solution followed by filtration into a HPLC vial through a $0.45\ \mu\text{m}$ filter. The measurements were performed with a mixture of chloroform/hexafluoro-2-propanol (HFIP) as solvent (98/2 $\text{CHCl}_3/\text{HFIP}$). The flow rate was 0.8 ml/ min at a constant temperature of 20°C .

Dynamical mechanical analysis was performed on a TA Instruments Q800 device. The applied temperature range was -120 to 150°C with a heating range of $2^\circ\text{C}/\text{min}$. The applied

experimental method was tensile mode with a fixed strain of 5 μm at a frequency of 10 Hz. The tensile arrangement was chosen due to the sample thickness (~ 1 mm).

Thermogravimetical analysis was performed on a Shimadzu DTG60 device in a temperature range of room temperature to 600°C under oxygen atmosphere.

The applied *thermal conductivity* test method was the following: a sheet specimen is introduced between two known-temperature references. Thermal power is calculated on the basis of the input electrical heating power at the higher temperature side (T_1). Based on this heat flow and thermal gradient can be calculated and finally their quotient is the coefficient of thermal conductivity.

Electrical conductivity was determined via the 4-point resistivity test. Sensors were placed at 20 mm intervals.

Both *small and wide angle X-ray diffraction* was performed on pCBT and graphene-modified pCBT sheets. Radiation was CuK alpha in reflexion mode. Crystalline layer distance was calculated according to Bragg's law.

Optical microscopy pictures were taken of the cross-sections of the composites by an Olympus BX51M optical microscope equipped with Canon Camedia C5060 digital camera with AnalySIS software.

For *scanning electron microscopy* studies the broken surfaces of the specimen were first gold plated by a JEOL FC1200 fine coater device in argon atmosphere then pictures were taken of the surface by a JEOL 6380LVa scanning electron microscope.

Transmission electron microscopy (TEM) was utilized to study the dispersion of the graphene nanoplatelets in the pCBT matrix. The TEM device (Zeiss LEO 912 Omega) was working at an acceleration voltage of 120 kV. Thin specimens (50 nm) were prepared by ultramicrotome (Leica EM UC6, Wetzlar, Germany) cut with a diamond knife (Diatome, Biel, Switzerland).

3.2.2. Mechanical tests

Mechanical tests were performed to analyze the properties of the composites produced and to study the effect of the modifying agents.

Tensile tests were carried out by a Zwick Z005 universal tensile tester (Zwick/Roell GmbH, Ulm, Germany) according to EN-ISO 527 standard with a crosshead speed of 20 mm/min in case of the unreinforced specimen.

Interlaminar shear tests

Static interlaminar shear tests were performed on a Zwick Z020 (Zwick/Roell GmbH, Ulm, Germany) universal tensile tester according to ASTM-D 3846-94 standard with a test speed of 1.3 mm/min.

Dynamic interlaminar shear tests were performed on a Ceast Resil Impactor Junior instrumented pendulum equipped with a DAS 8000 data collector according to EN-ISO 8256 standard with specimen according to ASTM-D3846-94 standard. The impact energy was 15 J, and pendulum speed was 3.7 m/s.

Flexural tests were performed by a Zwick Z020 (Zwick/Roell GmbH, Ulm, Germany) universal tensile tester according to the standard EN-ISO 14125 at a deformation speed of 5 mm/min. The span length applied was depending on specimen thickness and the type of the reinforcement. The width of the specimen were 15 mm in every cases.

Instrumented *Charpy dynamic impact tests* were performed on a Ceast Resil Impactor Junior with a DAS 8000 data collector device according to EN-ISO 179 standard. The applied energy was 15 J and span length was 62 mm for the unnotched type I samples.

Fiber content (weight percentage) was determined by ashing the matrix in a Nabertherm furnace heated to 600°C for 30 minutes according to the standard EN-ISO 3451.

3.3. Sample preparation

3.3.1. Samples for characterizations

Samples for characterization experiments were produced in a hot press (Collin P200E) at 240°C. Polymerization time was 15 min under 2 MPa pressure and 1 mm thick sheets were obtained by this method.

Additives (polycaprolactone and graphene) and CBT was melt-mixed in a Brabender PlastiCorder PL 2000 type mixer at a temperature of 200°C, and at a revolution speed of 180 min⁻¹ for 2 minutes. Then this mix was fine-grinded in a blender. The mix was hot-pressed according to the above written parameters.

3.3.2. Composite samples

Prepreg method

Prepreg manufacturing: CBT powder was dispersed onto the carbon weave (Figure 1/a). Then this structure was put into a preheated (195°C) oven for 1 min to melt the CBT powder. Due to its low viscosity and capillary action the molten CBT flowed among the fibers. After 1 min the prepreg was taken out of the oven and cooled down to ambient temperature (Figure 1/b).

This caused the ROP to stop and the prepreg to be ready. Due to frozen ROP, this prepreg has theoretically unlimited shelf life with a non-sticky surface which makes storage easy.

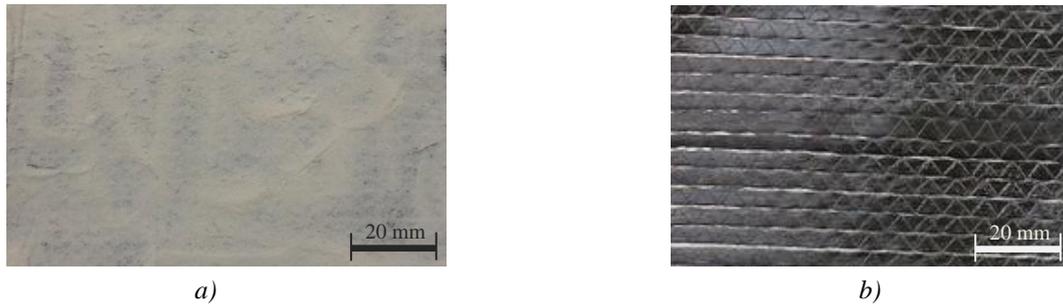


Figure 1. Production of prepregs: CBT powder dispersed on UD carbon fiber weave (a), prepreg sheet (b)

Composites were produced from the above described prepregs via *hot consolidation*. A composite structure was built up by 8 layers of prepregs with the orientation of $(0/90^\circ)$. This structure was put into a hot press preheated to 240°C . Pressing time was increased to 15 min. Composite sheets were obtained by this method with a thickness of ~ 1.5 mm and a fiber mass fraction of $\sim 60\text{wt}\%$ (result obtained according to EN-ISO 3451 standard).

Modifying agent (polycaprolactone) was added to the pCBT after drying and a powder mixture was made in a blender. Since initial viscosity was not increased by PCL, appropriate impregnation was achieved and PCL modified matrix composites were produced via the above described method.

Premix method

Graphene and CBT were melt-mixed in a Brabender PlastiCorder PL 2000 type mixer at 200°C , 180 min^{-1} for 2 minutes which do not affect polymerization – see ‘Torque curves’ chapter. Then this mix was fine-grinded in a blender. The fine powder was dispersed onto the reinforcement then a new layer is placed onto the first layer and powder mix is also dispersed onto it. In this way 8 layers are built up and placed into the preheated hot press and pressed for 15 min at 240°C and 2 MPa pressure. This method resulted in ~ 2 mm thick composite sheets with an average fiber mass fraction of $\sim 60\text{wt}\%$ (result obtained according to EN-ISO 3451 standard).

4. New scientific results - Theses

1st thesis

I proved by differential scanning calorimetry (DSC) studies, that at least 50°C/min cooling speed is necessary to obtain a tough, sub-40% crystalline polymerized cyclic butylene terephthalate (pCBT) matrix composite. Due to the fast cooling the molecules cannot be ordered into a perfect crystalline structure, so the polymer becomes less rigid [2, 3, 4, 7].

2nd thesis

I proved by rheology and gel permeation chromatography that cyclic butylene terephthalate (CBT) is suitable for a continuous composite processing technology. Since the ring-opening polymerization reaction takes place after impregnation, the viscosity of the matrix after ring opening until the start of the polymerization remains low (0.02-0.05 Pas) and it starts increasing only after the start of polymerization [1, 3, 4, 6].

3rd thesis

I supported by dynamic mechanical analyses empirically and by the application of Fox equation theoretically the already known, but not necessarily proven fact, that CBT and polycaprolactone (PCL) copolymerize, which is shown by the shift in the glass transition peak. I proved by DSC studies, that due to the above copolymerization, crystalline fraction of the material decreases, which increases toughness. Toughening is also supported by tensile tests: adding 10 wt% PCL increases tensile strain by 600%. Parallel to this, PCL increased significantly the dynamic interlaminar shear strength of the carbon fiber reinforced composites by 25% since the matrix film between the reinforcing layers has been toughened [7].

4th thesis

I proved that the nucleation effect of graphene is prevailed in the ring-opening polymerizing CBT, since after adding 5 wt% graphene, crystallization peak rises from 189°C to 202°C at 10°C/min cooling speed due to heterogeneous nucleation, so supercoolability of CBT decreases if graphene is present in the melt. I also proved, that graphene increases initial viscosity parallel to heat- and electrical conductivity in the range of 0-5% weight proportion. The reason of the latter is a network structure of graphene in the pCBT matrix, which increases electrical conductivity by ten magnitudes to 1 mS/cm and heat conductivity with 80% to 0.21 W/mK [5].

5th thesis

I proved that the presence of 0.5 wt% graphene increases the static interlaminar shear strength of carbon fiber reinforced pCBT matrix composites, since the propagating cracks in the matrix have to get around the graphene particles in the matrix. Above 0.5 wt% a reverse phenomenon takes place: at higher nanoparticle contents agglomerates are present which may act as weak points and be origins of cracks [5].

5. List of own publications

Publications in periodicals

1. **Balogh G.**, Czigány T.: Design of a pultrusion device (in Hungarian). *Gép*, **60**, 3-6 (2009).
2. **Balogh G.**, Czigány T.: Effect of air humidity on the mechanical properties of in-situ polymerized cyclic butylene terephthalate matrix composites. *Materials Science Forum*, **659**, 1-5 (2010).
3. **Balogh G.**, Czigány T.: Effect of low UD carbon fibre content on mechanical properties of in situ polymerised cyclic butylene terephthalate. *Plastics, Rubber and Composites*, **40**, 121-124 (2011). IF=0,257
4. **Balogh G.**, Czigány T.: Cyclic butylene terephthalate (CBT) as a novel matrix material and its processing (in Hungarian). *Műanyag és Gumi*, **48**, 234-240 (2011).
5. **Balogh G.**, Hajba S., Development of cyclic butylene terephthalate matrix graphene and carbon fiber reinforced hybrid composites (in Hungarian). *Műanyag és Gumi*, (accepted, in press: expected publication: June 2012).

Conference proceedings

6. **Balogh G.**: Development of thermoplastic matrix pultrusion technology, Reinforced Plastics 2010. International Balaton Conference, Keszthely, Hungary, 2010. 05. 18-20. CD Proceeding p4.
7. **Balogh G.**: CBT as a novel matrix material and its processing techniques for composites. SPE Eurotec Conference. Barcelona, Spain, 2011.11.14-15. p. 1-5, online proceeding (2011).

Conference presentations

8. **Balogh G.**, Szaplóczay P.: Application of pultruded composites in high voltage wires. Reinforced Plastics 2008. International Balaton Conference, Keszthely, Hungary, 2008. 05. 20-22.
9. **Balogh G.**, Czigány T.: Effect of air humidity on the mechanical properties of cyclic butylene terephthalate composites. VII. Hungarian Conference on Materials Science, Balatonkenese, Hungary 2009. 10. 11-13 (poster presentation)
10. **Balogh G.**: Development of thermoplastic matrix pultrusion technology. Reinforced Plastics 2010. International Balaton Conference, Keszthely, Hungary, 2010. 05. 18-20.
11. **Balogh G.**: CBT as a novel matrix material and its processing techniques for composites. SPE Eurotec Conference. Barcelona, Spain, 2011. 11. 14-15.