SIMULTANEOUS BINDING AND TOUGHENING CONCEPT FOR TEXTILE REINFORCED IN SITU POLYMERIZED CYCLIC BUTYLENE TEREPTHALATE COMPOSITES

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1 Introduction
The growing interest in textile reinforced thermoplastic composites has made considerable efforts that have been devoted on the processing technology based on in situ polymerized Cyclic Butylene Terephthalate (pCBT). However, the brittleness problem of pCBT after isothermal polymerization and crystallization is a significant disadvantage that hinders its application. Various potential toughening approaches such as copolymerization with polycaprolactone [1] or tetrahydrofuran [2] have been attempted to overcome the brittleness problem of pCBT. The resulting copolyesters showed indeed increased toughness. The mechanical properties such as stiffness and strength, however, were found to be decreased in these copolyesters. Further attempt with physical modification by adding carbon nanotubes (CNT) was conducted as well [1]. The stiffness and strength were found to be increased due to the reinforcement by the CNTs. Nevertheless the CNTs filled pCBT shows little increase in toughness. In this research, a new concept consisting of binding and toughening is therefore proposed for manufacturing of textile reinforced pCBT composites. Specifically, textile preforms with preforming binder are prepared first for enhanced handling stability and improved process efficiency. After impregnation of the bindered textile preforms with liquid catalyzed CBT oligomers, the textile reinforced pCBT composites are manufactured successfully at isothermal conditions. The unique of this process is that the textile reinforced pCBT composites can be efficiently manufactured and qualifiedly toughened simultaneously due to the tailored preforming binder.

2 Experimental

2.1 Materials

2.1.1 Matrix system
pCBT®500 in granular shape, which is purchased from Cyclic Corporation (Schwarzheide, Germany), was used in this study. Before processing, the oligomers were dried overnight at 80 °C in order to remove moisture which could interfere with the polymerization reaction according to the processing guide provided by Cyclic Corporation. The catalyst used in this work was liquid FASKAT® 4102 (Butyltin tris-2-ethylhexanoate, CAS # 23850-94-4) and powder TEGOCAT 256 (butyl(oxo)tin, CAS# 51590-67-1).

2.1.2 Preforming binder

Tab. 1. Activation conditions of the employed preforming binders.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Temperature (°C)</th>
<th>Duration (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOTADEL® AX8090</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>EPIKOTE® Resin 05390</td>
<td>90</td>
<td>30</td>
</tr>
<tr>
<td>PARALOID EXL® 2314</td>
<td>150</td>
<td>30</td>
</tr>
</tbody>
</table>

Three kinds of preforming binder were used in this study. The first is epoxy binder EPIKOTE® Resin 05390 from Hexion special chemicals was chosen because of the fact that the possible reaction between PBT and epoxy resin system can lead to a tougher PBT according to [3, 4]. The other two binder systems, PARALOID EXL® 2314 based on acrylic modifier from DOW Germany and LOTADEL® AX8090 based on a random terpolymer of ethylene (E), methyl acrylate and glycidyl methacrylate (GMA) from Arkema France, are commercial impact modifier systems for thermoplastic polyester resins. The
activation conditions of the three preforming binder are illustrated in Tab. 1.

2.1.3 Textile reinforcement

Three kinds of textile reinforcements were applied in this research. A uni-directional fabric PANEX35 from ZOLTEK and biaxial non crimp fabric S32CX from Saertex were used for the development and evaluation of the processing system. The third textile reinforcement is a triaxial non crimp fabric manufactured by ITA (RWTH Aachen) in the frame of the allied DFG-AfF-Cluster project “Light weight and textiles”. The areal weights and fiber orientations of the textile reinforcements were summarized in Tab. 2.

Tab. 2. Material properties of textile reinforcement

<table>
<thead>
<tr>
<th>Textile reinforcements</th>
<th>Area weight [g/m²]</th>
<th>Fiber orientations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uni-directional carbon fabric</td>
<td>333</td>
<td>0</td>
</tr>
<tr>
<td>Biaxial non crimp carbon fabric</td>
<td>530</td>
<td>±45°</td>
</tr>
<tr>
<td>Triaxial non crimp glass fabric</td>
<td>1374</td>
<td>+45/-45/90</td>
</tr>
<tr>
<td>Triaxial non crimp glass fabric</td>
<td>1374</td>
<td>90/-45/+45</td>
</tr>
</tbody>
</table>

2.2 Methodology

2.2.1 Influence of compaction temperature on the compaction behavior of bindered textile preforms

A lab based binding process, which can be applied for both powder and granulate form preforming binders, was developed to prepared bindered textile preforms. The textile reinforcement used in this study is A1 and A2 with a symmetric configuration [+45/-45/90]. The bindered textile preforms were prepared using EPIKOTE® Resin 05390 binder and cut into compaction test sample after activation of the binder. The samples were tested under controlled temperature conditions. A preload of 400 Pa was used for the compaction experiment. The whole compaction process was divided into three stages which are compaction, holding deformation and release based on the position control.

2.2.2. Influence of binder on the thermal and rheological properties of matrix system

Rheological properties

DSC measurements were performed on DSC Q2000 device from TA Instrument. Experiments were run with samples ranging from 7 to 10 mg in the sealed aluminum under nitrogen to prevent moisture and oxidative degradation. The effect of preforming binder on the simultaneous polymerization and crystallization phenomenon of the catalyzed CBT oligomers was analyzed with samples prepared by mixing the materials, including CBT500, preforming binder, and the liquid FASCAT4102 catalyst with melt blending process. The samples were rapidly equilibrated to 190 °C at a heating rate of 100 °C/min and held at that temperature isothermally until the heat flow trace goes back to baseline. Since the polymerization of pCBT from CBT is essentially athermic [5], the exothermic peak during the isothermal process is considered as the crystallization of pCBT.

Thermoplastic Vacuum Assisted Resin Infusion

To prepare textile reinforced pCBT composites at isothermal conditions, the traditional VARI process for thermoset resins should be modified according to the processing characteristics of reactive processing of thermoplastics. The modified VARI for thermoplastic oligomers should include commonly following features: (1) A resin melting, mixing, and transfer unit with a heating capacity up to 205 °C. The catalyst should be mixed with CBT500 homogeneously without dramatic temperature fluctuation before resin infusion. The transfer unit should provide a constant temperature environment so that the resin cannot be cooled down or overheated during transfer; (2) A heated molding plate with a heating capacity up to 205 °C, which can be used for
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isothermal production conditions; (3) A suitable mold release agent or demolding concept for non-destructive and easy demolding with a good surface finish; (4) A temperature resistant (up to 205 °C) and economical flexible mold (vacuum bag), if possible, also reusable; and (5) A controlled temperature environment for polymerization reaction.

Verification of the simultaneous binding and toughening concept

Epoxy resin binder EPIKOTE® was chosen for the preparation of the bindered textile preforms. After manufacturing, the flexural properties of the textile reinforced pCBT composites were determined on a universal material testing machine (Zwick GmbH Co. KG, Ulm) using three point bending test according to ASTM D790. A 2.5 kN load cell was integrated to measure the flexure force at a loading speed of 3.41 mm/min. For each laminate, five specimens for the flexural test were conducted to ascertain the effect of material and test system variability. The flexural modulus, the flexural strength, and especially the flexural strain at break which indicates the toughness of the laminate were investigated. Single factor analysis was performed to study the influencing mechanism of a single process parameter on the flexural properties while other process parameters being held constant. A higher flexural strain at break while the flexural modulus and flexural strength are not significantly changed is considered as the optimal performance for the textile reinforced pCBT composites.

2.2.4 Influence of preforming binders on the interlaminar fracture properties

To assess the influence of preforming binder on the interlaminar fracture properties, three kinds of preforming binder were used for preparation of textile reinforced pCBT composites. Interlaminar fracture toughness of textile reinforced pCBT composites was investigated under mode I deformation. A standard double cantilever beam (DCB) test was applied to evaluate the mode I fracture toughness. The effect of binder type, filling content and preparation concept on fracture properties were discussed on the basis of morphology analysis of fracture sections with scanning electric microscopy.

2.2.5 Influence of toughening concept on the flexural properties

According to the results from 2.2.4, the preforming binder, which leads to the optimum interlaminar fracture properties, was applied in this study to evaluate the influence of various toughening concepts on the toughening performance and mechanical properties. In situ toughening, ex situ toughening, and the combination of the two methods were considered. The purpose of this experiment is to combine the advantages of in situ and ex situ toughening concept. The advantage of in situ concept is global toughening that the matrix of the whole laminate can be toughened. The problem is the increase of the matrix viscosity and the decrease of mechanical properties. The ex situ toughening (i.e. the proposed concept in this paper) is local toughening that specially applied for the weakest interply regions of the laminate. The mechanical properties of the laminate cannot be significantly altered due to the matrix of the inner laminate regions is not greatly influenced, which is also the reason for limited toughening.

3 Results and discussion

3.1 Influence of compaction temperature on the compaction behavior of binder textile preforms

The compaction temperature represents a positive effect on the Fiber Volume Fraction (FVF) as indicated Fig. 1, where the relationship between FVF and compaction pressure was record under various compaction temperatures. As shown in Fig. 1, although there are meanwhile effects from preforming parameters (Binder activation temperature and binder activation time), the FVF indicates an obvious increase with increasing compaction temperature under the same compaction pressure. It is believed that the effect of compaction temperature on the FVF can be related to the four material state of the binder. Because the four selected compaction temperatures correspond to the four material states of the binder, which is solid (level 1, 25 °C), partly melted (level 2, 60 °C), fully melted higher viscous (level 3, 125 °C) and fully melted lower viscous (level 4, 190 °C). The compressibility of the bindered textile preforms can be tailored by the compaction temperature due to the fact that the re-organization of the fibers can be facilitated by the lubricating effect from the melted preforming binder.
3.2 Influence of binder on the thermal and rheological properties of matrix system

3.2.1 Simultaneous polymerization and crystallization

One of the advantages of CBT resin based technology for textile reinforced thermoplastics is that the production process can be isothermal at temperatures lower the melting point of pCBT (about 225 °C) without any thermal cycle. Therefore, the simultaneous polymerization and crystallization phenomenon during isothermal production process is of great importance that should be studied.

The effect of preforming binder on the simultaneous polymerization and crystallization of FASCAT4102 catalyzed CBT500 at 190 °C is shown in Fig. 2. For all of the tested samples only one exothermic crystallization peak was observed during the isothermal stage of about 30 min. The presence of preforming binder significantly changes the simultaneous polymerization and crystallization phenomenon of the FASCAT4102 catalyzed CBT500 system. One of the distinct influence due to the addition of preforming binder is the starting time of crystallization of the FASCAT4102 catalyzed CBT500 at 190 °C. Compared with sample without addition of preforming binder (0 wt. %) the addition of 2 wt. % to 6 wt. % leads to an earlier crystallization. The polymerization of CBT oligomers to pCBT polymer with sufficient high molecule weight seems to be accelerated due to the addition of epoxy resin based preforming binder including epoxide functional groups which can react with pCBT [3, 4].

3.2.2 Rheological properties

For the rheological analysis the TEGOCAT256 (0.4 wt. %) catalyzed CBT500 matrix system was used for its medium reaction rate and easy sampling by powder blending. Fig. 3 illustrates the typical variation of viscosity and phase angle with time for the selected matrix system measured isothermally at 190 °C. The curves can be classified into four typical zones according to the phase transition depicted by the phase angle curve. Zone I in the first 25 min indicates the melting and stabilizing of the matrix system. The scattered phase angles in this zone contributed by the different portion of CBT oligomers in the matrix system as observed in the DSC investigation on the CBT oligomers. The melted portion of CBT oligomers indicates a very low average complex viscosity of 0.05 Pa s. Zone II between 25 min and 31 min is the stabilized matrix system with a phase angle of 90 °C, indicating a purely viscous (Newtonian) fluid nature. The processing window indicated in the Figure across Zone I and Zone II is usually defined for LCM processes for evaluation of the processability of the applied resin system. This is according to the fact that a resin viscosity lower than 1 Pa s is generally taken as the appropriate processing viscosity for good impregnation of textile fibers [6, 7]. Zone III between
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31 min and 50 min reflects an abrupt phase change from a purely viscous (Newtonian) fluid to a nearly elastic solid with a phase angle of about 2°, indicating a drastic change in viscoelastic behavior in the matrix system. Along with the abrupt phase change, the viscosity of the matrix system increases rapidly from 10 Pa s up to 106 Pa s due to the fast nature of the ring-opening polymerization. Zone IV between 50 min and 60 min illustrates the end stage of the reaction, where both the phase angle and the complex viscosity remain fairly stable as a result of the completely consolidated sample in the measurement geometry. The effect of binder filling content on the processing time was investigated in the case of epoxy resin binder. For both FASCAT4102 and TEGOCAT256 catalyzed CBT500 resin, the processing time is found to be prolonged with increased preforming binder.

3.3 Development of the manufacturing process

3.3.1 Thermoplastic Vacuum Assisted Resin Infusion (T-VARI)

A schematic representation of the developed T-VARI system is show in Fig. 4a. The CBT500 granulate is melted (175-185 °C) in a heated aluminum cup on a magnetic stirrer. After pouring the catalyst into the resin melt, the mixture is stirred by a rod rotating in the magnetic field for about 10 seconds. Then the resin infusion process is started with a defined vacuum pressure and mold temperature. The resin transfer tube (Silicon) goes through a heated L shape copper tube with a diameter greater than the resin transfer tube. The copper tube is closed with two covers and silicon tube, with iron powder filled inside in order to provide an isothermal temperature equal to the resin temperature so that the resin can neither be cooled nor over heated during transfer. A full vacuum of -850 mbar is applied during the polymerization reaction. The mold temperature is held constant for a scheduled time for the polymerization reaction. Two Teflon plates with a thickness of 1 mm are used in the experiment: one of them is between the laminate and the mold surface for easy demolding and the other is between the laminate and the vacuum bag for improving the surface quality of the final plate. A reusable vacuum bag (Silicon film with a thickness of 1 mm) is applied to reduce the production cost. The porous fleece is used to stop the flow front timely, so that the vacuum could be held with a reusable unheated hose at the outlet side until the polymerization reaction is finished. Fig. 4b and 4c show the developed processing system and a triaxial glass fabric reinforced pCBT laminate manufactured with the manufacturing system. The result indicates that the developed infusion process can achieve a good 1-dimensional infiltration of textile preforms, which is essential for analyzing the homogeneity of composite
properties such as the variation of mechanical properties along the infiltration direction.

The impregnation quality of the textile reinforced pCBT composites was observed under optical microscope using unidirectional fiber reinforced pCBT samples. An overview of the cross section of the sample with a magnification of 200 times is illustrated in Fig. 5. In general the unidirectional fibers are impregnated very well by the low viscous CBT resin, leaving only a few macro bubbles in the interply region. Those macro bubbles may be caused by the dual scale flow effect during infiltration. Further observation in the fiber bundles was performed with a magnification of 1000 times as shown in the upper left corner of Fig. 5. Most of the fiber filaments are covered by pCBT matrix, meaning a good impregnation quality. However, a small amount of micro bubbles were observed among the fiber filaments as well. These bubbles may be included during the mixing of catalyst or infiltration because of the unbalance resin flow in the textiles. Generally, the results indicate that the performance of the developed T-VARI manufacturing process and the properties of the manufactured composite materials in this research are satisfactory and comparable to the process developed in [8].

3.3.2 Verification of the simultaneous binding and toughening concept

Fig. 6 indicates a typical flexural stress-strain relations of textile reinforced pCBT laminate prepared with or without applying simultaneous binding and toughening concept. Both of the two composite laminate shows a brittle failure before yielding as illustrated in Fig. 6. The brittle nature inherent in the composite laminate based on pCBT matrix was not completely eliminated with the proposed concept. However, the composite laminate does exhibit a great improvement of flexural strain at break. Compared with the reference laminate, an increase of 74.2% in flexural strain at break was observed for the textile reinforced pCBT laminate prepared with the proposed concept. The expected simultaneous toughening of interply region was achieved with the applied EPIKOTE® Resin 05390 preforming binder. Most importantly, the toughening performance was obtained without impairing other mechanical properties. On the contrary, an increase of 69.6% in flexural strength was observed and the flexural modulus was not significantly altered.

The effect of various toughening concepts on the toughening performance was further analyzed according to the flexural test results, accompanied by the analysis of their influence on the mechanical properties. The toughening performance was characterized by the value of the flexural strain at break. The mechanical performance was assessed by the values of the flexural modulus and the flexural strength. Tab. 3 illustrates the flexural test results from a control laminate without any toughening effort,
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laminates prepared according to in situ toughening concept and laminates fabricated with simultaneous binding and toughening concept (quasi as ex situ toughening concept).

Tab. 3. Effect of simultaneous binding and toughening concept on the flexural properties of textile reinforced pCBT composite

<table>
<thead>
<tr>
<th>Concept filling fraction</th>
<th>Binder [wt. %]</th>
<th>Flexural modulus [GPa]</th>
<th>Flexural strength [MPa]</th>
<th>Flexural strain [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>0</td>
<td>26.5±2.5</td>
<td>420.7±21.1</td>
<td>1.59±0.07</td>
</tr>
<tr>
<td>In situ</td>
<td>2</td>
<td>25.1±4.5</td>
<td>506.7±54.7</td>
<td>1.94±0.12</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>26.4±2.8</td>
<td>532.8±25.1</td>
<td>1.99±0.12</td>
</tr>
<tr>
<td>Ex situ</td>
<td>2</td>
<td>28.7±0.9</td>
<td>711.6±31.4</td>
<td>2.75±0.15</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>21.5±1.7</td>
<td>347.3±11.1</td>
<td>1.69±0.32</td>
</tr>
</tbody>
</table>

The results show that both in situ and ex situ toughening concept have great potential in toughening of textile reinforced pCBT composites. Compared with the control sample, in situ toughening with 2 or 4 wt. % leads to an improvement of about 18 % in flexural strain. The flexural strength was improved by 26.7 % in the case of 4 wt. % preforming binder. The flexural modulus, however, was nearly not changed. As for the ex situ toughened variants, the toughening potential was only observed with 2 wt. % preforming binder in the interply region, which illustrates an excellent toughening performance with an increase of 72.9 % in flexural strain, 69.1 % in flexural strength, and even 8.3 % in flexural modulus respectively. An increase of preforming binder up to 4 wt. % seems to have a negative influence on the toughening performance and mechanical properties. No significant improvement of flexural strain was observed and both flexural modulus and flexural strength were greatly reduced compared with the control laminate.

The toughening performance of both in situ and ex situ toughening concept for textile reinforced pCBT composites may be ascribed to the influence of preforming binder on the simultaneous polymerization and crystallization process of pCBT polymer matrix in the composite laminate. For the in situ toughening concept, the pCBT polymer matrix was toughened globally since the preforming binder was directly mixed with the CBT resin before infiltration. There will always be interactions between the preforming binder and the catalyzed CBT oligomers during manufacturing, including the infiltration and the followed isothermal polymerization and crystallization process. In the case of ex situ toughening concept, however, the pCBT polymer matrix was toughened locally since the preforming binder is mainly located in the interply region of the composite laminate. The interaction between the preforming binder and the catalyzed CBT oligomers is limited in the interply region and occurred primarily during isothermal polymerization and crystallization stage. This is because that the low viscous CBT oligomer melt tends to impregnate the intraply region first due to the lower flow resistance when compared with the interply region which is partly blocked by the preforming binder.

3.4 Influence of preforming binder on the interlaminar fracture properties

3.4.1 Mode I fracture toughness

The relationship between applied load and crack opening displacement (COD) for the specimens are shown in Fig. 7. The results indicate that the applied load and the COD are both influenced by the toughening concept and binder filling content. For the ex situ toughened specimens the applied binders also show an effect on the applied load and especially for the COD. The specimen ex situ toughened with PARALOID EXL® 2314 results the highest COD of all the tested specimens. As the stiffness is not significantly influenced by the ex situ toughening, the increase of COD may indicate that the specimen has higher resistance to fracture and that the PARALOID EXL® 2314 binder might be the most appropriate binder for toughening of textile reinforced pCBT composites.

In order to make a better comparison, an overview of the results from all the tested specimens prepared with ex situ toughening concept, including the final fracture toughness (Δu = 40) and the sample thickness is shown in Fig. 8. The first row of x-axis in the graph is the specimen number from 1 to 3 along with the resin infiltration direction. The second row of x-axis is the filling contents of the applied binders. And the third row indicates the applied binder type. The thickness of all the specimens is shown in the second y-axis to determine whether there is an influence from the thickness variation on the results.
of mode I fracture toughness. The results indicate that there is an intra-part thickness variation for all tested laminates and this variation does not result clearly a corresponding variation of mode I fracture toughness. Therefore, for the pre-selection of binders with DCB test, a repeatability test, which is very helpful due to the common inter-part thickness variation in VARI process, was not considered in this study.

Fig. 7. Load displacement trace from DCB test

As we can see in Fig. 8, for the eighteen specimens with LOTADEL® AX8900 and EPIKOTE® Resin 05390 binder, the mode I fracture toughness is usually lower than 400 J/m² except for the 4 specimens marked with the arrows in the graph, each of which shows much higher mode I fracture toughness than the other two specimens which has very close results from the same laminate (Fig. 8). Therefore, for the comparison these 4 specimens are excluded here because of the huge inter-specimen deviation. This might be attributed to the errors such as the not in-plane-justified metallic hinge occurred during the specimen preparation. After comparing with the reference laminate whose mode I fracture is in a range of 500 ~ 800 J/m² (Fig. 8), the binders LOTADEL® AX8900 and EPIKOTE® Resin 05390 can be removed from the selection list due to the decreased mode I fracture toughness.

In this case, the PARALOID EXL® 2314 would be the only choice in the present study for the proposed simultaneous binding and ex situ toughening concept. Actually, for the nine specimens with PARALOID EXL® 2314 binder, the mode I fracture toughness is indeed higher than the specimens with the other binders at the same loading conditions. An exception are the two specimens with 3 wt. % PARALOID EXL® 2314, which is still comparative with the best results available from the other two binders (Fig. 8). This further confirms the initial conclusion that the PARALOID EXL® 2314 might be the most appropriate binder according to Fig. 7. Of all the three filling content for PARALOID EXL® 2314, the 7 wt. % specimen shows the best performance in the aspect of homogeneity. In addition, the specimens filled with 7 wt. % PARALOID EXL® 2314 also show more homogeneous mode I fracture toughness than the reference laminate.

3.4.2 Fracture surface of mode I deformation

Fig. 9 shows the SEM images of the fracture surface on textile fiber reinforced pCBT laminates with various binders derived from DCB tests. As shown in Fig. 9a, the reference laminate indicates a typical brittle fracture from mode I deformation. The brittle pCBT matrix breaks into pieces around the fiber after mode I deformation. The effect of the three different binders on the mode I deformation are shown in Fig. 9b, c and d. The fibers are not with adhesion of polymers in the case of pCBT/AX8090 laminate, indicating that the LOTADEL® AX8090 binder is not compatible with pCBT, such that the resulted matrix does not stick to the fibers very well (Fig. 9b). Although the EPIKOTE® Resin 05390 shows a better compatibility with pCBT matrix compared with LOTADEL® AX8090, the toughness of the resulted matrix in the interface represents only incremental enhancements (Fig. 9c). After comparing Fig. 9d with Fig. 9a-c, an obvious difference in the interface of the pCBT laminate with the PARALOID EXL® 2314 binder was observed. Not only a good adhesion between the fibers and the matrix is present, but the fracture surface indicates a clearly plastic deformation, meaning that the brittle pCBT matrix at the interlayer of the pCBT laminate is greatly toughened by the introduction of PARALOID EXL® 2314 binder.
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Fig. 8. The final mode I fracture toughness and thickness of all the tested specimens

(a) Reference laminate
(b) pCBT/AX8090 3%
(c) pCBT/5390 3%
(d) pCBT/2314 3%

Fig. 9. Scanning electron micrographs of the fracture surface under mode I loading of textile fiber reinforced pCBT laminates
3.5 Influence of toughening concept on the flexural properties

For further improvement of the performance of the proposed concept, a combination of in situ toughening concept and ex situ toughening concept was tried in order to achieve a tailored global toughening performance. Specifically, a small amount of binder used additionally as in situ toughening agent which is directly mixed with CBT oligomers melt in order to toughen the pCBT matrix in the intraply region. The amount of binder as in situ toughening agent should be as low as possible so that the flow properties of the matrix resin and the mechanical properties composite would not be negatively influenced. The bindered textile preforms with 2 wt.% preforming binder was still applied for toughening of interply region. Tab. 4 illustrates the results of the modified simultaneous binding and toughening concept. The two binders, EPIKOTE® Resin 05390 and PARALOID® EXL2314, were applied in the experiment with 0.5 and 1.0 wt.% of each binder as in situ toughening agent.

Tab. 4. Effect of toughening concept on the flexure properties of textile reinforced pCBT composite

<table>
<thead>
<tr>
<th>Preforming binders</th>
<th>Toughening concepts</th>
<th>Flexural modulus</th>
<th>Flexural strength</th>
<th>Flexural strain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[GPa]</td>
<td>[MPa]</td>
<td>[%]</td>
</tr>
<tr>
<td>NONE</td>
<td>—</td>
<td>26.5 ± 2.5</td>
<td>420.7 ± 21.1</td>
<td>1.59 ± 0.07</td>
</tr>
<tr>
<td>PARALOID® 2314</td>
<td>Ex-situ</td>
<td>28.1 ± 2.3</td>
<td>801.6 ± 25.9</td>
<td>3.34 ± 0.29</td>
</tr>
<tr>
<td></td>
<td>CombII*</td>
<td>31.2 ± 1.3</td>
<td>705.4 ± 55.1</td>
<td>2.78 ± 0.27</td>
</tr>
<tr>
<td></td>
<td>CombII**</td>
<td>32.7 ± 1.7</td>
<td>689.5 ± 68.1</td>
<td>2.39 ± 0.22</td>
</tr>
<tr>
<td>EPIKOTE® 05390</td>
<td>Ex-situ</td>
<td>28.7 ± 0.0</td>
<td>711.6 ± 31.4</td>
<td>2.75 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>CombI</td>
<td>30.8 ± 1.5</td>
<td>715.8 ± 11.7</td>
<td>2.77 ± 0.26</td>
</tr>
<tr>
<td></td>
<td>CombII</td>
<td>30.9 ± 3.6</td>
<td>657.0 ± 59.9</td>
<td>2.28 ± 0.21</td>
</tr>
</tbody>
</table>

*Comb: Ex-situ 2 wt.% plus In-situ 0.5 wt.%
**CombII: Ex-situ 2 wt.% plus In-situ 1 wt.%

Constant process parameter
→ Catalyst amount: 5 wt.%; Processing temperature: 185 °C
→ Vacuum pressure: -800 mbar; Polymerization time: 90 min

The results indicate that the flexural modulus from the four modified variants remains nearly unchanged as before. However, different performance in flexural strength and flexural strain were observed for the two binders with modified concept. For the PARALOID® EXL2314 binder, both the flexural strength and flexural strain were found to decrease when the in situ toughening part of binder increases from 0.5 wt.% to 1 wt.. The flexural strength and flexural strain results from the two modified variants are 12 % and 16.7 % lower than the pure ex situ toughening variant. For the EPIKOTE® Resin 05390 binder, an addition of 0.5 wt.% binder as in situ toughening agent leads to nearly the same flexural strength and flexural strain in comparison with the pure ex situ toughening variant. Further increase of in situ toughening agent up to 1 wt.% results to a decrease of flexural strength and flexural strain as well.

The different performance of the two binders in the modified concept may be attributed to the difference of the two binders. The EPIKOTE® Resin 05390 is a low melting point epoxy resin which have a good compatibility with CBT oligomers at lower filling content so that the infiltration behavior is not significantly influenced. Therefore, a filling content of 0.5 wt.% with in situ concept gives almost the same results as the pure ex situ toughening variant. The PARALOID® EXL2314 binder is a rubber powder with well-defined particle size which remains unchanged during in situ mixing with CBT oligomer melt according to the product description. As a result, only a little amount as low as 0.5 wt.% can already increase the viscosity of the mixture, leading to a poor impregnation quality.

4 Summary

In this work, a new concept consisting of binding and toughening simultaneously has been proposed for an efficient and qualified manufacturing of textile reinforced pCBT composite. Research emphasis has been put on the following three aspects: (1) Materials characterization focus on the effect of preforming binder on the compaction behavior of textile preforms as well as the thermal and rheological behavior of catalyzed CBT oligomers; (2) Process development including T-VARI manufacturing process and single factor analysis of the processing conditions; and (3) Process optimization in terms of the performance of various preforming binders and the toughening concept. To summarize, the toughening of textile reinforced pCBT composites has been successfully achieved with simultaneously improved process efficiency by introducing simultaneous binding and toughening concept.

References

SIMULTANEOUS BINDING AND TOUGHENING CONCEPT FOR TEXTILE REINFORCED IN SITU POLYMERIZED CYCLIC BUTYLENE TEREPTHALATE COMPOSITES


