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Adhesion problematics and curing kinetics in a thermosetting matrix for stitch-free non-crimp fabric

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Abstract

Non-crimp fabrics (NCF) have become established in the fields of the automotive, aircraft, and wind power industries, which has led to an increasing demand of fiber plastic composites. In order to utilize the known excellent load-bearing properties of NCF and also to reduce the related disadvantages such as fiber undulation caused by stitching yarn, inclusions of resin and filament breakage by the stitch-bonding process have to be addressed. Hence, an alternative manufacturing technology is presented. This technology is defined by the punctiform application of a polyester hot melt adhesive to enable different geometries of NCF and ensure the position of the high-performance fiber in the load direction. The new manufacturing process, on the one hand, demands new testing methods to investigate the adhesion between the used adhesive and high-performance fibers, while, on the other, the surface of the adherend (carbon fiber) needs to be improved. Oxyfluorination is used here for the surface modification. Different tests such as peel test, shear test and transverse tensile test were developed and evaluated with different adhesives and high-performance yarns based on glass and carbon. The influence of the used copolyester hot melt on the curing kinetics of an epoxy matrix was investigated by differential scanning calorimetry using quasi-isothermal and non-isothermal measurements. In addition, the interface between the thermoplastic epoxy resin and the copolyester hot melt was analyzed by scanning electron microscopy.

Keywords

stitch-free non-crimp fabric, differential scanning calorimetry, polyester copolymer, maximum detachment force, hot melt adhesive, oxyfluorination

Non-crimp fabrics (NCF) based on carbon or glass fibers are mostly impregnated by epoxy resins to be used as fiber-reinforced composites in the field of the aerospace and automotive industry. They exhibit a large potential for application as primary load-bearing structures. The NCF are currently manufactured by bonding the different layers of unidirectional high-performance yarns, such as carbon fibers, with a stitching yarn. These fibers are set according to the load direction of the prospective structural elements and produced in a multiaxial warp-knitting machine.¹ The machine working process in the production of NCF leads to disadvantages in the existing NCF, such as fish-eyes, resin inclusions, gaps or ducts in the component structure, as shown in Figures 1 and 2. This has led to demand for studies regarding the crack behavior as well as in the development potential of alternative manufacturing process.^{2,3} Though it was also shown

that the channels of stitching respectively at the stitching yarn enhance the permeation of resin in fabrics, the damaged individual filaments of the fiber caused during the penetration of the sewing needle influence the in-plane properties of composites and leads to a reduction in the mechanical properties before any impact.^{4–6}

In order to avoid the aforementioned failures and disadvantages of NCF, basic research has been carried out at the Institute of Textile Machinery and High

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Figure 1. A polished cross-section of a four-layered multi-axial warp knitted fabric, recorded in bright-field mode, showing three ducts.

Figure 2. A polished cross-section of a four-layered multi-axial warp knitted fabric, recorded in bright-field – dark-field mode and showing a duct respectively gap between carbon fiber bundle caused by the warp knitting yarn.

Performance Material Technology (ITM), Technische Universität Dresden for developing a novel technology suited for large-scale production to produce a novel stitch-free non-crimp fabrics (SF-NCF).⁷ This newly developed ink-jet processing based technology enables different layers of fabrics to be bonded by local application of adhesives between the layers without stitching yarn. Unlike the existing technologies where the bonding of different UD (unidirectional) layers using a laminar binder, such as binder tapes, mat of fibers, or powders, takes places as an additional processing step after the knitting or consolidation process (stitch bonding), this technology enables an inline punctiform binding of the yarns locally so that highly drapable fabrics

can be produced.^{8,9} Here the fish-eyes are completely eliminated and the entire load properties of the SF-NCF can be utilized through fully elongated high-performance yarns.

There also exist other methods or techniques that are being currently researched using adhesive for manufacturing textile, such as chemical stitching. In the chemical stitching process, thermosetting adhesive and polyamide nonwoven are used to improve the pre-form and their fixing process.³ Besides the fixation, it also aims to improve the infiltration behavior of glass fiber wovens and achieve adjustable draping properties and stiffness. However, minimal fiber undulation still occurs after the vitrification of the adhesive due to their tubular form, resulting in the formation of adhesive columns. Also the thermal fixation might be disadvantageous in case of carbon fibers. Since the amount of binder in the textile needs to be much less than 4%, as it significantly influences the mechanical properties,⁷ the adhesion behavior of the fiber with respect to their surface properties plays a decisive role in determining the amount of binder to be used and hence needs to be studied. This research focuses on studying the adhesion behavior of carbon fibers and their curing kinetics for this new technology in order to determine whether a surface treatment of the carbon fibers improves the adhesion properties so that a new generation of highly adaptable freedom SF-NCF with a higher degree of freedom can be produced. Carbon fibers do not exhibit a high surface functionality – they are chemically inert. It is therefore important to increase the adherence to possible matrix systems by an applied sizing or surface functionalization. Also, often the sizing is removed by mechanical stress of the yarn such as the guiding rolls and sizing can age. In both cases, the functionality of sizing to improve the adherence gets reduced and further treatment is needed. This study is highly relevant in order to determine the suitability of this technology for producing fabrics with extremely low adhesive contents. In this technology, a thermoplastic polyester copolymer suited for thermosetting plastic is used to glue/bond the different fiber layers together.

It is well known that the existing good properties of highly cross-linked epoxy resins, e.g. high mechanical strength and young's modulus as well as solvent and heat resistance, are enhanced by different types of additives used.¹⁰ Therefore, it is well suited to be used with the novel SF-NCF as semi-finished product for fiber-reinforced plastics. Due to this, the influence of the adhesive onto the epoxy resin has to be known: firstly, for the curing of the epoxy matrix, secondly, for the resulting interfaces between fiber–adhesive and fiber–resin, and, thirdly, for the intrinsic properties as phase separation in the epoxy resin.

Also the curing kinetics of an epoxy resin can be easily influenced by such components as adhesive. As a result additives can be used to influence the impact resistance of fiber-reinforced plastics or to generate a higher stiffness,¹¹ electromagnetic properties, or a superior toughness.^{12,13} These elements can be either nanotubes made of carbon or polyamide,^{14–17} as well as nanoclay and thermoplastic inclusions.¹⁸ Consequently, the used copolyester hot melt also affects the curing reaction of the epoxy resin and the mechanical properties of the subsequent thermosetting fiber-reinforced plastic. Accordingly, the effect of these hot melt particles on the curing behavior of the epoxy resin needs further attention and investigations at the micron scale.

In general, epoxy resins are widely used as adhesives, coatings, and reinforcing materials. Epoxy resin is mixed with rubbers and thermoplastics for toughening the brittle and highly cross-linked material.¹⁹ Hence, many investigations were carried out to examine the curing kinetics after the addition of thermoplastics. These examinations were done mostly after the insertion of highly-branched polyesters which are added to improve the surface energy of the blends,²⁰ or to be used as known toughening agent for epoxy resin.^{13,21,22} Every epoxy system exhibits its own curing characteristics and operating temperatures depending on the composition of the resin themselves and the hardener components. In this work, a further component was added in the form of adhesive in the semi-finished product and has to be investigated regarding the altered curing kinetics. The experimental investigation is carried out by quasi-isothermal and non-isothermal differential scanning calorimetry. It has to be considered that a further component does not only influence the terms of curing but also influences the mechanics and properties of a fully cured semi-finished product. Therefore, in this work, the polyester copolymer is used to manufacture non-crimp fabrics by gluing the several unidirectional layers of carbon fibers. Here, the polymer has two functions: Firstly, to join the fabric and secondly, to improve the stability of the fiber-reinforced plastic. Based on their usage, different aspects have to be investigated: at first, the interface between the high-performance fibers and the adhesive is evaluated by single fiber tensiometry and drop shape analysis. Here, the enhancement of surface energy by surface treatment through oxyfluorination was taken in account. Additionally, these investigations are compared with achieved maximum detachment force determined by the novel testing set up for the peel and shear force. Second, the influence of the adhesive onto the used curing kinetics of epoxy resin is necessary to examine. For this, the differential scanning calorimetry is used quasi-isothermal and non-isothermal. Furthermore, the effect of adhesive onto the epoxy resin structure the fractured surface is studied using a scanning electron microscope. As a

result, the received information will be used to estimate the influence of the adhesive during the manufacturing process of a resulting fiber reinforced plastic. The fraction behavior and mechanical properties of the fiber-reinforced plastics could be then explained by this information.

Material and methods

Material

EpikoteTM resin MGS[®] RIMR 135 from Hexion (MomentiveTM, Columbus, US) based on bisphenol A is used as epoxy resin. The resin is mixed with the EPICURETM Curing Agent MGS[®] RIMH 137 based on alkyl ether amine and isophorone diamine (MomentiveTM, Columbus, US). Both products are commercially available and widely used.

The hot melt adhesive used for the study is polyester Co-Polymer CE 21 and purchased from EMS-Chemie AG, Swiss. It can be used as granulate, powder or suspension for the production of the SF-NCF. In order to study the curing kinetics, a powder which is further processed in cryogenic mill with a grinding ball diameter of 25 mm (Mixer Mill 200; Fa. Retsch, Haan, Germany) is used. The powder is treated at a temperature of 196°C at 30 Hz for 30 s. The E-modulus of the CE 21 hot melt adhesive determined by a four-point bending test is 11.7 MPa. Furthermore, a polyolefin hot melt B 4147.2 from the Bühnen GbmH (Bremen, Germany) is used as granulate for adhesion studies. The operating temperature lay between 150°C and 170°C with a viscosity around 1400 mPa s. Both hot melts can be applied with the pressurized-jet CT valve micro-dosing system (Liquidyn, Sauerlach, Germany).

Carbon fibers (CF) and Glass fibers (GF) were used in this study. The used CF were HTS 45 E23 (epoxy sizing), HTS 40 F13 (polyurethane sizing), and UMS 40 F23 (polyurethane sizing), produced by Toho Tenax Europe GmbH, Germany. The diameter of the used carbon fibers is approximately around 6.3 µm (calculated by light microscope measurements). The glass fibers (GF) used were EC 600 350 and EC 600 354 with different silane sizings supplied by P-D Glasseiden Oschatz GmbH, Germany. In comparison to CF, GF has an amorphous structure. CF based on polyacrylonitrile (PAN) is one of the most common high-performance fibers used for fiber polymer composites and for various applications in automotive, construction sectors. CF exhibit excellent load bearing properties and has an anisotropic graphite lattice.²³ In general, the surface chemistry of CF is often driven by the applied sizing. Without such a sizing, the CF of defined by acidic surface groups like carboxylic and hydroxyl groups.^{24,25}

Manufacturing of SF-NCF

The implementation of the new technology was realized on laboratory scale for closed multi-layer NCF samples made of glass and carbon fibers. The nozzle system was mounted on a Kuka robot KR 6-R900 for a free positioning of adhesive dots in the NCF structure. Different dot patterns, orientations and different penetration depth were realized. A statistically defined pattern exhibits the best two-dimensional solidification without affecting the draping properties. The orientation of the NCF layers (0° , 90° , and $\pm 45^\circ$), also determine the statistical distribution of the adhesion pattern. It is also possible to enable certain geometries by a specified and punctual application of adhesive to ensure a better adaptability of the received novel, stitch-free NCF. The use of this technique allows an adjustment of the number of dots and the depth of dot insertion. The manufactured SF-NCF of four layers contains approximately 99,600 dots per m^2 . The used hot melt suspension needs to be thermally activated. The heating was realized by heat plates with the dimension of $450\text{ mm} \times 450\text{ mm}$ and with a defined pressure. As a consequence of the use of suspension of CE 21, the achieved mass of an adhesive dot is between $2.7\text{ }\mu\text{g}$ and $3.5\text{ }\mu\text{g}$. The application of such small amounts became necessary since a single yarn consists of approximately 12,000 single filaments with $7\text{ }\mu\text{m}$ to $18\text{ }\mu\text{m}$ diameter, which have to be fixed in place.

Sample composition and particle size

The particle size and the sample composition were investigated in the micron range via a scanning electron microscope (SEM). The measurements were performed using a high-resolution low-voltage SEM (Zeiss DSM 982 Gemini, Germany). A field emission cathode was used. The microscope sample plate was wrapped with tin foil and subsequently coated by a mixture of thermoset matrix composed of epoxy resin and hardener with different amounts of polyester hot melt particles (0 wt%, 1 wt%, 5 wt%, and 10 wt%). The samples were cured out in an oven at 80°C . Finally, they were cut in half to investigate the fractured surface and their intrinsic properties. Furthermore, the adhesive hot melt particles were located on a SEM disc. Based on the received SEM images, the particle size was calculated the by Axio Vision SE 64 Rel. 4.8 software. The particle size was estimated by the longest chord of two contour points.

Differential scanning calorimetry

The thermal analyses are done using a differential scanning calorimeter (DSC) from TA Instruments Q2000

TzeroTM DSC for quasi-isothermal and for non-isothermal measurements. Nitrogen was used as purge gas with 50 mL/min . The instrument calibration was performed using sapphire (Tzero calibration) and indium (flow rate, temperature). The samples were analyzed in a hermetic aluminum pan and exhibit a sample mass of epoxy resin of $11.6 \pm 1.2\text{ mg}$. The samples were prepared with different ratios of adhesive compared to the complete mass of matrix, for which the weight percent ratios of adhesive were 0%, 1%, 5%, and 10%. The samples were gently homogeneous mixed and were prepared freshly before every measurement. The mixing ratio of resin to curing agent amount was 100:30.

The quasi-isothermal measurements were performed at 80°C for 250 min. The sample was placed in the chamber when the certain isothermal temperature was reached. The non-isothermal experiments were done at different heating rates of 2 K/min (amplitude 0.212 K). The temperature curve was driven from 0°C to 230°C . Before the non-isothermal measurements, the chamber was cooled to -30°C to ensure that there was no pre-curing reaction.

Further, the glass transition temperature (T_g) of the quasi-isothermal cured samples was determined from the reversible heat flow. The first cycle was run from 0°C to 230°C while the other cycles (2nd to 5th) were measured with a heating rate of 2 K/min . The fifth heating cycle of post curing was used to determine the final glass transition temperature ($T_{g,\infty}$).

The conversion x was calculated in consideration of the complete curing reaction: The exothermic heat during the chemical reaction can be seen as proportional to the number of functional groups in the investigated resin.²⁶ Therefore, the total conversion x can be calculated as follows:²⁶

$$x = \frac{\Delta H_t}{\Delta H_{tot}} \quad (1)$$

In this work, ΔH_t is the reaction enthalpy until the time t measured under quasi-isothermal conditions at 80°C . This is divided by the ΔH_{tot} which is the overall reaction enthalpy for a full reaction performed by a non-isothermal DSC measurement at 2 K/min . For the calculation of ΔH_{tot} , it is necessary to ensure a completed reaction. With isothermals measurement below the glass transition temperature, a full conversion could not be achieved.²⁶

Incineration

Incineration was used to determine the amount of used adhesive to manufacture a novel NCF made from glass fibers. The experiment was done according to the standard procedure.²⁷ The samples were taken

from unconsolidated NCF without stitching yarn (reference) and with applied, activated adhesive suspension CE 21. A Nabertherm muffle furnace B170 (Nabertherm GmbH, Germany) was used to burn up the samples at 625°C for 1 h in a porcelain pan. The samples were weighed before and after the calcination process. With respect to the used adhesives, the measurements were performed with sample containers containing lid to avoid hazardous gases. There was a threefold determination of each sample. The reference was a NCF with four layers of glass fibers and without stitching yarn. To calculate the mass (wt%) of adhesive in the NCF the residual amount of the reference was subtracted from the residual amount of the glued NCF.

Surface functionalization of carbon fibers

Oxyfluorination of carbon fibers

The oxyfluorination was done at Fluor Technik System GmbH in Lauterbach, Germany. Batch process is used in which sized carbon fibers were functionalized for 10 min at room temperature. The fluorine gas concentration was 5% and the pressure of the reaction chamber was reduced to a pressure of 200 hPa. After the processing, the chamber was flushed with fresh air and evacuated several times to eliminate the remaining fluorine gas. The fluorine gas was fed to a calcium carbonate chamber where it was converted to calcium fluoride. Afterwards, the samples can be removed.

Influence on the surface energy

The surface tension describes the wettability properties of a substrate as high-performance fibers (CF and GF) and the adhesive (CE 21 E). To estimate the surface tension of the fiber material, the contact angle θ was determined to calculate the surface energy γ according to:

$$\frac{\gamma_l(1 + \cos \theta)}{\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p \left(\frac{\gamma_l^p}{\gamma_l^d} \right)} + \sqrt{\gamma_s^d} \quad (2)$$

This method is based on that developed by Owens, Wendt, Rabel, and Kaelble.²⁸

Using this model, individual filaments can be evaluated in their wettability. The contact angle is a parameter of the degree of attraction of the liquid by the substrate and gives the levels of hydrophobicity. The surface tension is composed of the polar component (p) and the disperse component (d). Dipole-dipole interactions, hydrogen bonds and acid-base interaction affect the polar component. The disperse component is defined by van der Waals forces.²⁸ The tensiometer used was a Krüss K 100 (Krüss GmbH, Germany).

Influence on the maximum force of detachment

In order to evaluate the degree of adhesion between two high-performance yarns, a test was developed to determine the maximum detachment force.^{29,30} The samples glued together were specially prepared. During the sampling, the fibers were assembled at the end by a ferrule and had a certain length in elongated orientation. They were joined by two different adhesives such as polyolefin hot melt B 4147.2 and polyester hot melt Griltex CE 21. Three different types of stress can be evaluated using these methods: peel test, shear test and transverse tensile test. In order to measure the maximum force of detachment after peel or shear stress, the samples have to be prepared in a parallel position and were wrapped around the sample holder (Figure 3). The samples for the transverse tensile test have to be prepared in an orthogonal direction. A P-jet CT nozzle system (LIQUIDYN GmbH, Germany) was used to apply the adhesives in the high-performance yarns on a custom made sample holder. To ensure a steady conditions, an even contact force of 10 N was used. Specially prepared sample holders for a tensile testing machine Z2.5 with a nominal load of 2.5 kg were developed to perform the three stress tests. This experimental set-up was implemented according to Figure 3(a) and (b): peel test and shear test.

Figure 3. Experimental set-up for measuring the maximum force of detachment: (a) peel test and (b) shear test.²⁹

Table 1. Surface energies of high-performance yarns and used adhesives

		$\gamma_{s, \text{total}}$ [mN/m]	γ_s^p [mN/m]	γ_s^d [mN/m]
EC 600 350	Glass fiber	53.4	9.3	44.1
EC 600 354	Glass fiber	36.1	2.9	33.2
HTS 40 F13	Carbon fiber	43.3	9.7	33.6
HTS 40 F13, oxyfluorinated	Carbon fiber	57.5	18.4	39.1
HTS 45 E23	Carbon fiber	39.9	6.5	33.4
HTS 45 E23, oxyfluorinated	Carbon fiber	53.2	14.9	38.3
UMS 40 F23	Carbon fiber	45.9	10.7	35.2
UMS 40 F23, oxyfluorinated	Carbon fiber	59.0	12.8	46.2
Griltex® D 2351 E CoPES (CE 21)	Copolyester hot melt	37.55	6.9	30.65
Bühnen B 4147.2	Polyolefin hot melt	22.6	0.6	22.0

Results and discussion

Adhesion properties

The adhesion properties are related to different aspects such as to the surface energies of the used components themselves, i.e. the adhesives and the high-performance yarns, and of the surface functional groups which were provided by the different sizing of the yarns or from subsequent surface treatment like used oxyfluorination. With respect to the polarization theory for adhesion of De Bruyne,³¹ polar functional groups must be provided by both adherend. Therefore and in order to study the adhesion capability, the surface energies are determined via single fiber tensiometry for the high-performance yarns and with a drop shape analysis system for the cured out adhesives. The results are shown in Table 1.

In order to ensure an acceptable adhesion between two adherends, the surface energy of both components should be comparable.³¹ Also, the number of the surface functional groups is important. Accordingly, the surface energy of the adhesive has to be at least as high as the surface energy of the bonded high-performance yarn in Table 1. After the oxyfluorination, the surface energy of sized carbon fiber types gets improved by a significant increase of the polar part of the surface energy which leads to assume to get a better adhesion. For the ultra-modulus carbon fiber UMS 40 F23, the polar part rises by 19.63%. For the both high-tensile carbon fibers the polar surface energy increases by 89.7% (HTS 40 F13) and 129.2% (HTS 45 E23). Caused by the reason, the fibers were not desized before; the oxygen during the fluor gas-phase reaction can react with the existing sizing components which were based on polyurethane (HTS 40 F13 and UMS 40 F23) or epoxy (HTS 45 E23). Thus, novel polar functional groups as --COOH appear as well as oxygen is bound as --C--O-- and --C--O--F--H groups on the surface.³⁰

In relation to the measured maximum forces of detachment, there is a characteristic dependence to the developed testing setups. Due to the two different types of hot melt adhesive, there are explicit differences between the measured forces, and same measured behavior pattern in the measured force for detachment are exhibited from both the tests. The two adhesives exhibit different amount of surface functional groups which can be seen at the polar part of the surface energy (Table 1). Both testing setups are newly developed and give information about usability of the method as well as to the suitability of the adhesive to carbon fibers and glass fibers. The lowest force measured is presented in Figure 4 for the peel test. In contrast to this, the determined maximum force of detachment (delamination) for the shear test (Figure 5) additionally exhibits a narrower standard deviation. The developed tests consider a variety of applied forces and functional loads to fibers and yarns. Besides the tensile forces which are mainly driven by the detachment geometry of the adhesive bond, the bending load of the fiber is also an influencing factor in the peel test. This leads to the low detachment forces for the peel test results and to the high shear test forces. With respect to the peel test, the deviations of the determined forces in relation to the yarn type shows a higher dependence to the testing geometries compared to the shear test set up.

In the peel test, the polyolefin hot melt exhibits a higher maximum force of detachment compared to the polyester copolymer hot melt for the glass fiber (EC 600 354) with its silane sizing. In contrast, the carbon fiber shows a better adhesion to the hot melt Griltex® CE 21, which also exhibits a higher polar surface energy than the polyolefin hot melt. In general, a better and higher resistance to detachment can be shown for carbon fibers (HTS 40 F13) glued with Griltex® CE 21. Comparing the surface-modified and the untreated yarns, there are differences concerning to

Figure 4. Maximum force of detachment determined via peel test.

Figure 5. Maximum force of detachment determined via shear test.

the amount of maximum detachment force for the peel test and the shear test. These different factors lead to a high variability in the increase of force. For the surface treatment via oxyfluorination, the improved adherence is best demonstrated by the shear test, as the main load is associated to the direction of fiber. There is an enhancement in the maximum force of detachment by

the factor of 1.1 for the polyolefin hot melt B 4147.2 and of 2.9 for the hot melt Griltex® CE 21 in the shear test, which reveals the high potential of the fiber surface modification by oxyfluorination and the type of hot melt.³⁰ In the peel test, the improvement of the maximum force of detachment is found for the polyolefin hot melt B 4147.2 by a factor of 3.8 and for the Griltex®

CE 21 hot melt by a factor of 1.8. Therefore, the indicative increase of the maximum force of detachment shows the utility of the surface modification, such as oxyfluorination, for carbon fibers to improve the adhesion properties for different kind of hot melt.

Figure 6. SEM image of the used hot melt particles.

Effects of adhesive in epoxy matrix

The particle size of this coarse-dispersion copolyester hot melt system ranges from 10 μm to 260 μm in which approximately 61% of the system is located from 40 μm to 80 μm . By the used of the cryogenic mill, the surface of the particles is rough fractured (Figure 6). The median of the system is 65 μm .

In order to estimate the influence of the adhesive, the interface of a cured system composed of adhesive in different ratios with the cured used epoxy resin was investigated via SEM (Figure 7). For the pure cured resin, an almost smooth and conchoidal fracture surface is noticed (Figure 7(a)). In the case of a small amount of adhesive as 1 wt% in the two component resin, there are small particles recognizable in the area of fracture (Figure 7(b)) which are also visible for the 5 wt% ratio (Figure 7(c)). But no phase separation effects are recognizable for the 5 wt% ratio. For the highest adhesive–resin ratio, a clear hot melt phase (particle) and the epoxy resin can be recognized by the presence of a conchoidal fracture surface of the resin and the amorphous surface from the hot melt particle. Here, a changed intrinsic structure was found:

Figure 7. SEM micrographs of the fracture surfaces of cured mixture of epoxy resin with different amount of adhesive: 0 wt % (a), 1 wt % (b), 5 wt % (c), and 10 wt % (d) ($T_{\text{cure}} = 80^{\circ}\text{C}$).

small pores appear at the fractured surface and there are gaps between the adhesive and the resin which are filled with adhesive bonds (Figure 7(d)).

These findings correlate to phase separation effects, which are described by Boogh and Manson.¹³ Here, the polarity of surface functional groups of the hyper-branched polymer is sufficiently to influence the curing behavior by interfering during the opening reaction of the epoxy resin. It can be assumed, that the used copolyester adhesive exhibits enough surface functional

Figure 8. Phase separation effects – SEM micrograph of the fracture surface of cured mixture of epoxy resin with 10 wt % adhesive ($T_{\text{cure}} = 80^{\circ}\text{C}$).

groups as carboxyl groups and slightly more hydroxyl groups which lead the explained reactivity with the epoxy resin. This phase separation effects are shown in Figure 8. It is possible that a better impact behavior can be expected with a higher amount of polyester hot melt adhesive in the thermosetting resin caused by particle solidification and better energy absorption by the elastic adhesive particles. It was shown that the best toughening mechanism is induced by a second phase like particles.¹³

The glass transition temperature ($T_{\text{g}\infty}$) of a fully cured system is slightly affected by the contingent of adhesive. Pure epoxy resin exhibits a $T_{\text{g}\infty}$ of 90.8°C , which is close to the $T_{\text{g}\infty}$ of the lowest amount of 90.0°C for 1 wt%. With respect to higher amounts, the $T_{\text{g}\infty}$ rises for 5 wt% to 92.6°C and for 10 wt% to 94.5°C .

Figure 9 presents the heat flow signals per gram of resin as a function of the respective processing curing time. An acceleration effect is recognizable with increasing content of adhesive. The pure epoxy resin exhibits the exothermal maximum after 560 s and its profile demonstrates a typical autocatalytic behavior of an amino-cured epoxy resin based on a polyaddition.³² With an adhesive content of 1 wt% the reaction accelerates to 411 s and with an amount of adhesive of 5 wt% the reaction maximum is reached after 343.8 s. Moreover, there is a significant change in the curing time at 10 wt% with its acceleration of the reached exothermal maximum after 37.8 seconds. The curing

Figure 9. Influence of different amounts of adhesive in a RIMR 135 and RIMH 137 epoxy system to curing behavior. Heat flow ($T_{\text{cure}} = 80^{\circ}\text{C}$).

kinetics of an epoxy resin is diffusion controlled. With increasing amount of adhesive, there is an additional reactant which competes and reduces the mobility during the reaction of a bisphenol-A epoxy resin with the hardener components.³³ As a result, the chains of the epoxy resin become shorter and the reaction is earlier finished. If the curing takes place below the T_g , an incomplete conversion or limited conversion will occur.³⁴ Compared to the findings above, the conversion of the epoxy resin with 0 wt%, 1 wt%, and 5 wt% exhibits a similar final extent. The epoxy system with highest content of adhesive displays a lower final conversion, but the conversion at the start of the vitrification process is similar to the systems with lower amounts of adhesive.

Figure 10. Stitch-free non-crimp fabric of four layers of glass fibers consolidated by an activated hot melt adhesive suspension, polished section in weft direction, with small agglomeration of adhesive.

Figure 11. Non-crimp fabric of four layers of glass fibers without stitching yarn, polished section warp thread direction.

Properties of SF-NCF

In order to evaluate the quality of the manufactured novel SF-NCF, the amount of adhesive was determined by an incineration. The reference sample exhibits a residual amount after incineration of 0.58 ± 0.122 wt% which is mainly caused by the sizing of the glass fibers. After a fixation of a glass NCF with the suspension of CE 21, the residual amount increases to 1.00 ± 0.108 wt% which leads to an amount of adhesive in the manufactured NCF of approximately 0.42 wt% for a glass NCF with four layers. Following, the microscopically studies exhibit an easy penetration by the application needle, as shown in Figure 10. Small amounts of adhesive are visible as dark areas in the light microscope image.

With regard to Figure 11, the parallel orientation and non-crimped high-performance yarns due to the absence of a stitching yarn and even no ducts are recognizable. Due to the used developed technique to insert the activatable adhesive by a nozzle system, agglomeration of adhesive is visible in the insertion channel in the four-layered non-crimp fabric (Figure 10). It has been shown that such insertion channels enhance the consolidation behavior of dry, semi-finished textile fabrics in the z-direction.⁵ Other visible pore volumes and the uneven edge of the consolidated cross-section are caused by the sample preparation as well as the peel-ply. As aforementioned, channels caused by the stitching yarn support the infiltration of the matrix. With regard to the substitution of the stitching yarn by an adhesive, the infiltration channel occurs without a disturbing stitching yarn. On the one hand, the undulation of the high-performance fiber which may causes frictional stresses is avoided.⁶ On the other hand, there is no barrier caused by an additional yarn material in the insertion channels as shown for the inter bundle channels which are positioned horizontally between the different layers of a NCF.³⁵ The resulting ducts (Figure 10) are negligible compared with the gaps caused by stitching needles (see Figures 1 and 2).

Conclusion

In this research, different aspects were investigated, starting with the adhesion problematic using a newly introduced method for determining the maximum force of detachment and was successfully used to study the adhesion behaviors of glued high-performance yarns. Based upon the analysis it could be concluded that a surface treatment of the carbon fibers improves the adhesion properties. An efficient oxyfluorination of carbon fibers causes an increase in the polar surface energy and leads to an improved peel and shear behavior. Furthermore, the curing kinetics was studied to acquire first-hand information about potential change in the vitrification behavior of the used epoxy resin by

applied adhesive. It was shown that only with the highest content of adhesive at 10 wt% a significant change is exhibited, where the curing was accelerated and the conversion in the epoxy resin vitrification was lower. In addition, the investigations using SEM indicate a phase separation with the highest content of adhesive. Based on the results, the amount of adhesive ranging between 1 wt% and 5 wt% does not have any influence onto the curing kinetics and also does not show any phase separation effects. According to the final application needs and the novel technique to manufacture SF-NCF, the used amount of adhesive will stay under the found critical amount of 10 wt% in the epoxy resin. This was demonstrated by the incineration. The adaptation of the SF-NCF based on their application requires a thorough study of the influences for the amounts of adhesive in the range between 5 wt% and 10 wt% in order to obtain a comprehensive knowledge about the curing behavior and the potential phase separation. Also further studies are required to understand the influence of the adhesive on the mechanical properties of the resulting fiber reinforced plastics due to their polyester copolymer nature.

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