INTERFACIAL PROPERTIES OF CARBON FIBER REINFORCED POLYMER LAMINATES JOINED BY A NOVEL PARTIAL CROSS-LINKING PROCESS

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ABSTRACT

Direct bonding of partially cross-linked and freshly infiltrated resin parts represents a new concept for joining of thermosetting carbon fiber reinforced polymer laminates. Partial cross-linking maintains a particular chemical reactivity of the thermosetting resin which is used for bonding to a second, freshly infiltrated resin part. A final curing cycle guarantees complete cross-linking of the joined laminates, which are two plates in our investigation. For intermediate partial curing degrees of the first plate, excellent fracture toughness and a structured interface morphology of the joined laminates were found. The characteristic ripple-like resin surface structure of the partially cured first plate is maintained even after joining and final curing. It results from the peel-ply imprint and, before joining, represented the surface of the plate. In the present work the morphology and the micromechanical properties of this structured interface region of joined laminates are analyzed by microscopy and nanoindentation. The cross sections of a partially cured plate before joining and of a joined plate are investigated. Substantially reduced micromechanical modulus values are found within the interface region of the joined carbon fiber reinforced laminates. The changed material properties are confined to the ripple-like structures on top of the formerly partially cross-linked first plate. This mismatch of material properties together with the high contact area, resulting from the ripple-like surface structure of the first plate, seem to be responsible for the enhanced fracture toughness of samples joined by this new concept.

1 INTRODUCTION

The exceptional specific mechanical properties of carbon fiber reinforced polymers (CFRP) are responsible for their increasing importance in aerospace and automotive industry. For broader industrial application, joining of composite components is of high relevance to achieve a higher level of integral construction. Commonly, joining of thermosetting composite components is done by mechanical fastening with metallic bolts or blanks or by adhesive bonding [1, 2]. However, the required insertion of different materials and the creation of additional interfaces can be problematic and needs thorough processing.

An alternative joining concept for thermosetting CFRP laminates was proposed in our previous work and is based on direct bonding of partially cross-linked and fresh resin parts [3, 4]. The same liquid infusion resin system is used for both parts, in our investigation two plates. Thus no additional materials are used to yield the joint and thus common problems of other joining methods are avoided. Partial cross-linking of the resin can be realized by a thermal curing treatment at reduced temperatures and/or reduced curing times [5]. As only a moderate amount of polymer and hardener molecules are cross-linked, a particular reactivity of the thermosetting resin is maintained. Chemical reactions of the remaining functional groups with the fresh resin of the second CFRP part can take place and are utilized to join the partially cured and the fresh component. A final curing cycle of the joined parts guarantees complete cross-linking of the final component.

Intermediate partial curing degrees of the first plate between 70% and 80% are found to be promising for this new joining concept [4]. Improved failure behaviour resulting in high Mode-I fracture toughness values of the joined laminates are observed. The partially cured first plates are characterized by a ripple-like surface morphology after peel-ply pull-off, which exhibits a high contact surface and the possibility of mechanical interlocking. For the corresponding joined plates this ripple-like resin structure is preserved even after final curing, resulting in an inhomogeneous interface morphology with significant differences in the material properties.

In the present work a detailed microscopic and micromechanical analysis of cross sections of partially cured CFRP plates before joining (curing degree of 80%) and the corresponding joined plates is done. Modulus values are determined by nanoindentation. The high lateral resolution of this method allows an investigation of micromechanical parameters at different positions of the laminate's cross section. In particular, the structured interface region between the two joined laminates is analysed in detail and a determination of micromechanical properties of the ripple structure and their surrounding is done.

2 EXPERIMENTAL

2.1 Joining of partially cross-linked CFRP plates

The CFRP samples investigated in this work use the carbon fibers Tenax® HTA 40, distributed by the Toho Tenax Europe GmbH [6]. As polymeric matrix material the mono-component epoxy resin system HexFlow ® RTM6 is used, which is distributed by the Hexcel Corporation [7]. All HTA/RTM6 specimens were manufactured in a vacuum assisted resin infusion process using the VAP®-technique. The peel-ply textile WELA T0098 is used to assist in the VAP process.

A two-stage infiltration and curing process is used, as explained in detail in our previous work [4]. In a first step a CFRP plate with a partial curing degree of 80% is produced. A modified curing cycle at reduced temperature is used to obtain the defined partial curing degree of the RTM6 resin system [5]. As fiber reinforcement of the first laminate carbon fiber layers with stacking sequence (0/90)(0/90)(90/0)(90/0) are used.

In a subsequent step a dry fiber fabric of same stacking sequence is positioned on top of the first, partially cross-linked CFRP laminate, and infiltrated with fresh RTM6 epoxy resin. For final curing, this combination of partially cross-linked and fresh carbon fiber reinforced polymer is subjected to a final curing cycle at 180°C for 2.5 hours. The final curing transforms the partially cross-linked resin with a curing degree of 80% to a completely cross-linked resin further referred to as "80/100". The fresh resin system is completely cross-linked to a curing degree of about 100%. The resulting joined CFRP laminate thus is composed of a lower 80/100-part and an upper 100-part and in the following is labelled "80/100-100". The joined plates have a thickness of 5.7mm ± 0.2 mm.

2.2 Micromechanical analysis of CFRP cross sections

Micromechanical elastic moduli of resin regions of the partly cross-linked and the joined CFRP plates were measured by nanoindentation. During the loading-unloading indentation cycles the load-displacement curves F(h) are recorded. From the mainly elastic unloading curve the micromechanical parameters are quantified according to Refs. [8-10]. A detailed description of the method is included in our previous work [5].

The nanoindentation measurements were performed with a NanoTest 600 nanoindenter (Micromaterials Ltd.) and a Berkovich geometry indenter. The load controlled mode was used with loading and unloading rates of 2mN/s. In all measurements a dwell time of 5s was inserted between loading and unloading. Before analysis, the raw data of the load-displacement measurement is corrected by the system compliance. To determine the contact stiffness S, the unloading curve was fitted with a power law between $0.8 \cdot F_{max}$ and F_{max}. A Poisson's ratio of 0.35 is used [11]. Average modulus values were obtained by investigating comparable resin regions. The measurements were performed on plane cross sections of the CFRP samples, which were prepared by a grinding and polishing process. To investigate the micromechanical parameters of the resin of the CFRP plates as function of distance to the bottom of the plate, the position of the indents on the cross section was varied systematically from the bottom to the top.

All nanoindentation moduli are calibrated to modulus values of cured pure RTM6 epoxy resin samples with corresponding curing degree, i.e. curing degrees of 80% for plate 80 and 100% for the second part of plate 80/100-100. This is done to eliminate ageing effects of the resin, as the CFRP samples are investigated several months after production, which results in an increase of moduli [12].

2.1 Microscopic analysis of CFRP cross sections

Microscopic analysis of CFRP cross sections was performed by digital optical microscopy (Keyence GmbH, VHX-100). Microscopy was used to investigate the morphology of the surface of the partially cross-linked CFRP plate and the interface region of the joined CFRP plate.

3 RESULTS AND DISCUSSION

In the following the results of the microscopic and micromechanical investigation of the structured interface region of a joined 80/100-100 CFRP laminate are presented. For comparison also the corresponding partially cured plate 80 before joining is analysed. Joined laminates with this intermediate partial curing degree of the first plate are characterized by enhanced mechanical properties and unique behaviour of the interface region.

3.1 Microscopic analysis of the interface region of a joined 80/100-100 CFRP laminate

During CFRP production via VAP® the surface of the laminate is covered with a peel-ply textile, which assists in the removal of air and gas through a semi-permeable membrane system by the applied vacuum. In Figure 1a) the cross section of the partially cured CFRP plate 80 with the peel-ply textile at the top surface is shown. The fibers of the peel-ply with a diameter of (30.0 ± 1.3) µm are clearly visible and cover the topmost fiber and resin layer.

After the curing procedure, the peel-ply textile is pulled off. For CFRP laminates with intermediate curing degrees between 70% and 80%, complete peeling without resin adhesion is possible [4]. The imprint of the textile creates a regular, ripple-like pattern of the topmost resin layer, which defines the residual surface morphology of the partially cured CFRP plate. Figure 1b) shows the cross section of this surface structure of the partially cured CFRP plate 80. The diameter of the ripples is in accordance with the diameter of the textile fibers. A rough, periodically structured CFRP surface with high effective surface area is created, which is likely advantageous for bonding to a second laminate.

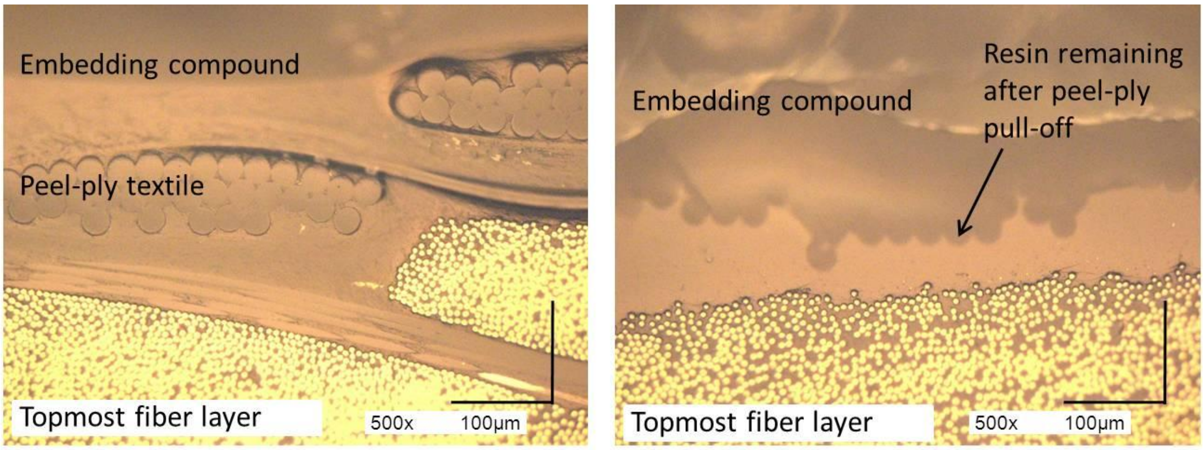

Figure 1: a) Surface region of partially cured CFRP plate 80 with peel-ply textile on top and b) after peel-ply pull-off.

During the joining process, the fresh resin infiltrates the dry fiber fabric of the second CFRP part on top of the partially cross-linked CFRP plate. Afterwards, the joined laminates are cured together in the final curing step. During this final curing process, the final morphology of the interface region develops. For the joined CFRP laminates with a partial curing degree of 80% of the first plate (called 80/100-100), the original, ripple-like surface structure of the partially cured first plate is preserved even after final curing. Cross-sections of the joined CFRP laminates show the typical imprint structures of the peel-ply textile within the 50-100µm wide resin interface region, as shown in Figure 2. Only limited intermixture of the partially cured and the fresh resin seems to occur during joining, favouring the observed inhomogeneous interface morphology.

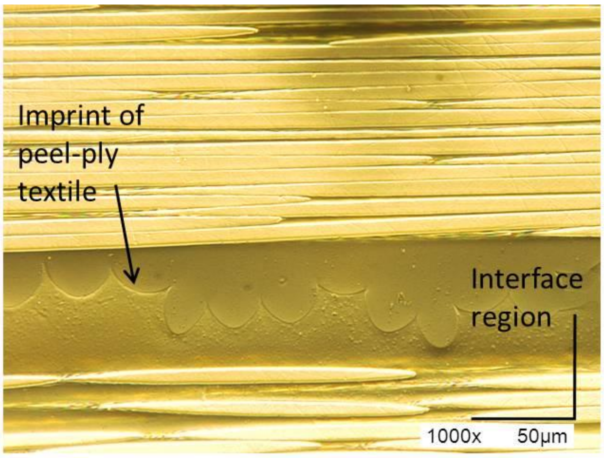

Figure 2: Cross sectional image of interface region of 80/100-100 laminate.

3.2 Micromechanical analysis the interface region of joined 80/100-100 laminates

In our previous work micromechanical scanning force (AFM) investigations of the cross-section of a joined 80/100-100 laminate revealed different modulus values of the resin structures within the interface region [4]. Again, the ripple like morphology is obvious. Significant differences in the AFM-modulus of the resin regions of the first plate (80/100) and the second plate (100) are measured, with the modulus of the first plate of about 20% smaller than that of the second plate. However, previous nanoindentation modulus measurements on pure 80/100 and 100 resin samples did not show these pronounced differences of material properties [5]. Possible reason for this discrepancy could be a change in surface properties of the partially cured first CFRP plate before or during joining, which does not affect the modulus of the resin within the bulk of the laminate.

To further investigate this problem, nanoindentation measurements of cross sections of the partially cured CFRP plate 80 and the joined CFRP plate 80/100-100 are performed. Resin regions at different positions of the cross-section are analysed, allowing a modulus investigation of the CFRP laminate as function of the distance to the bottom surface. In Figure 3 the cross-section of the partially cured CFRP plate 80 is shown. Positions of nanoindentation are marked by red circles. The positions 1 to 5 correspond to distances of 245µm, 560µm, 1115µm, 2075µm and 2945µm from the bottom surface of the CFRP plate.

In Figure 4 the corresponding modulus values of the partially cured first CFRP plate 80 are shown as function of distance from the bottom side.

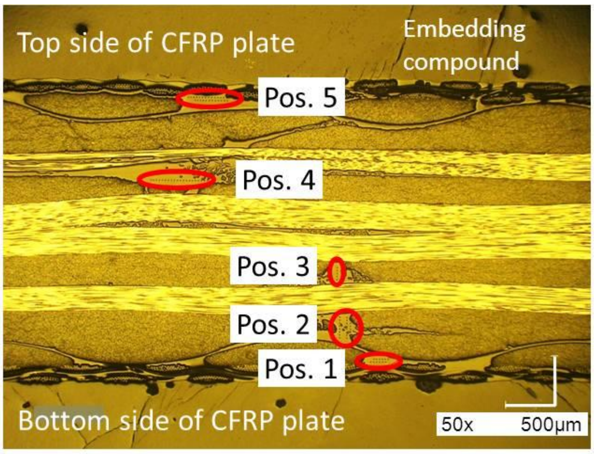

Figure 3: Indent positions 1 to 5 on cross section of partially cured first plate 80.

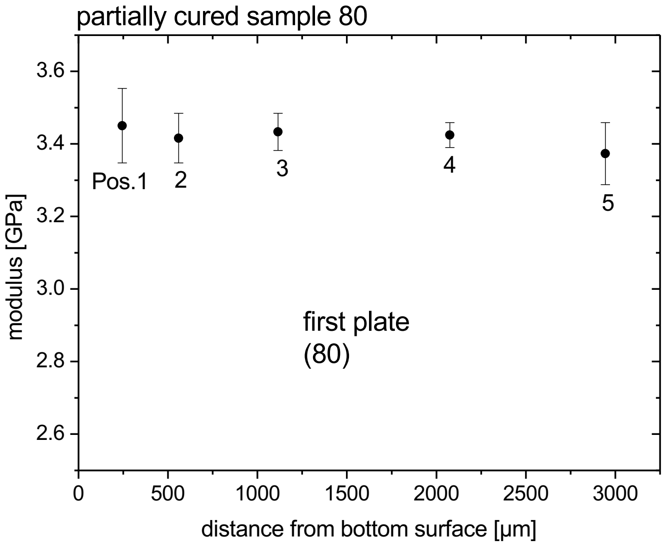

Figure 4: Modulus of partially cured first plate 80 as function of distance from the bottom surface.

The modulus values show no significant variations as function of distance from the bottom surface. They all range between 3.37GPa and 3.45GPa and are identical within their margin of error. In particular, no significant differences between moduli near the surfaces (position 1 and 5) and the bulk (positions 2 to 4) of the partially cured CFRP plate are found. Thus the surface of the partially cured

CFRP plate, which represents the contact area to the fresh resin during joining, shows no micromechanical modification in comparison to the bulk CFRP.

In Figure 5 the cross-section image of the joined CFRP laminate 80/100-100 is shown. Again the positions of nanoindentation are marked, which span the whole thickness of the sample. The positions 2 to 9 correspond to distances of 600µm, 1250µm, 1650µm, 2070µm, 2100µm, 2520µm and 2980µm from the bottom surface of the CFRP plate. The interface region of the joined laminates is located at a distance of 2050µm to 2150µm from the bottom surface, corresponding to positions 5 (ripple like structures on top of first plate 80/100) and 6 (resin at bottom second plate 100).

In Figure 5 the corresponding modulus values of positions 2 to 9 are shown as function of distance from the bottom surface. The range of the first plate, the second plate and the interface are marked in addition.

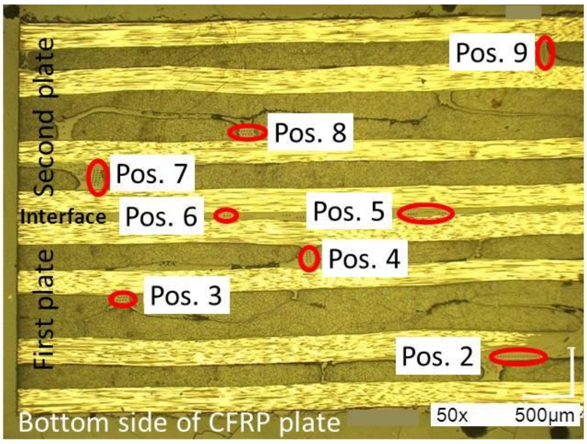

Figure 5: Indent positions 2 to 9 on cross-section of joined plate 80/100-100. The interface region is located in the middle plane of the sample at positions 5 and 6.

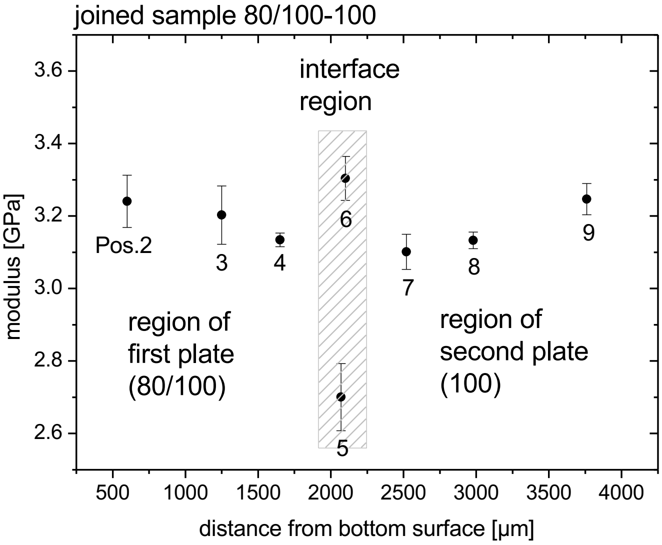

Figure 6: Modulus of joined plate 80/100-100 as function of distance from the bottom surface. The range of the first plate, the second plate and the interface are marked.

The moduli of the region of the first plate (80/100) agree well and range from 3.13GPa to 3.24GPa. Also the moduli of the region of the second plate (100) are in accordance and range from 3.10GPa to

3.25GPa. Besides, the moduli of first and second plate are in good accordance, which is in agreement with previous measurements on pure RTM6 epoxy resin (curing treatments 80/100 and 100) [5].

In contrast, within the interface region of the joined CFRP laminate 80/100-100 a significant mismatch of moduli is observed. The ripple-like structures on the first plate (position 5), which are of type 80/100, show a clearly reduced modulus value of 2.70GPa. The modulus is reduced by 18% compared to the average value of the bulk 80/100 region (positions 2 to 4). On side of the second plate (type 100) the resin of the interface region (position 6) shows a slightly increased modulus value of 3.30GPa as compared to the average value of the bulk of the second plate (positions 7 to 9). The increase amounts to about 5%. Thus within the interface region of the joined plates a mismatch of resin moduli of 22% exists, which is in good agreement to the previous AFM results [4]. This mismatch of micromechanical parameters is confined to the 50-100μm wide resin interface region.

Our investigation proves that the observed mismatch of micromechanical properties within the interface region of the joined 80/100-100 CFRP laminate must be a result of the joining and curing process. Before joining, the partially cured CFRP plate shows no significant variation of resin modulus. After joining, the interface region is characterized by a clear mismatch of moduli with a reduced modulus of the ripple-like structures on top of the formerly partially cured plate. The contact of partially cured resin and fresh resin and the curing treatment of both parts seem to result in a modification of the surface properties of the partially cured first laminate. Possible reasons are a limited intermixture of partially cured and fresh resin, a preferred adhesion of chemical species of the fresh resin on top of the partially cured laminate or a changed chemical composition of the surface of the partially cured plate due to oxygen absorption. All these reasons can modify the curing behaviour of the epoxy resin and result in modified micromechanical properties, which are confined to the direct contact zone of the two joined laminates. However, the inhomogeneous interface properties seem to be advantageous for the new joining concept, as the 80/100-100 sample exhibits superior failure behaviour and enhanced Mode-I fracture toughness [4].

4 CONCLUSIONS

Joining of partially cross-linked and freshly infiltrated epoxy resin represents a promising new joining concept for CFRP components. Partial cross-linking of the first CFRP part retains a certain chemical reactivity of the thermosetting resin, which is utilized for bonding to a second, freshly infiltrated CFRP part. A final curing step guarantees the complete cross-linking of the joined components.

Intermediate partial curing degrees of the first laminate between 70% and 80% have proven to be especially favourable. These partially cured plates are characterized by a ripple-like surface morphology after peel-ply pull-off. Within the contact zone of the joined plates this ripple-like structure is preserved even after final curing, resulting in an inhomogeneous interface morphology with significant differences in the material properties.

The presented investigations of the resin modulus in the cross-section of a joined 80/100-100 laminate by nanoindentation shows a mismatch of moduli within the interface region of first and second plate. The modulus of the ripple-like structures on top of the formerly partially cured first plate is significantly reduced by about 20% compared to the resin modulus of the second plate. The mismatch of moduli is confined to the 50-100μm wide resin interface region. The bulk properties of the two joined CFRP laminates are not affected.

The mismatch of material properties of the interface region together with the high contact area of the rippled contact zone seem to have positive effect on the joining quality, as the joined samples with intermediate curing degrees show enhanced Mode-I fracture toughness and improved failure behaviour. The results demonstrate the options of joining of partially cured and freshly infiltrated CFRP plates and the high potential of this new concept for direct bonding of CFRP components.

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REFERENCES

[1] Q. Bénard, M. Fois and M. Grisel, Influence of fibre reinforcement and peel ply surface treatment towards adhesion of composite surfaces, *International Journal of Adhesion & Adhesives,* **25**, 2005, pp. 404-409.

[2] S.T. Amancio-Filho and J.F. dos Santos, Joining of Polymers and Polymer–Metal Hybrid Structures: Recent Developments and Trends, *Polymer Engineering and Science,* 2009, pp. 1461-1476.

[3] M.G.R. Sause, L. Llopard Prieto, J. Scholler, S. Horn, J. Moosburger-Will and R. Horny, Patent DE 10 2011 010 384 A1.

[4] J. Moosburger-Will, M.G.R. Sause, R. Horny, S. Horn, J. Scholler and L. Llopard Prieto, Joining of carbon fiber reinforced polymer laminates by a novel partial cross-linking process, *Journal of Applied Polymer Science,* 2015 (doi: 10.1002/app.42159).

[5] J. Moosburger-Will, M. Greisel, M.G.R. Sause, R. Horny and S. Horn, Influence of partial cross- linking degree on basic physical properties of RTM6 epoxy resin, *Journal of Applied Polymer Science*, **130**, 2013, pp. 4338-4346.

[6] Toho Tenax Europe GmbH. Product literature to Tenax® HTA 40.

[7] Hexcel Company. Product literature to HexFlow RTM6®.

[8] J. Menčík, L.H. He and J. Němeček, Characterization of viscoelastic-plastic properties of solid polymers by instrumented indentation, *Polymer Testing,* **30**, 2011, pp. 101-109.

[9] W.C. Oliver and G.M. Pharr, Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology, *Journal of Materials Research,* **19**, 2004, pp. 3-20.

[10] B.J. Briscoe, L. Fiori and E. Pelillo, Nano-indentation of polymeric surfaces, *Journal of Physics D: Applied Physics,* **31**, 1998, pp. 2395-2405.

[11] C. Brauner, T.B. Block, H. Purol and A.S. Herrmann, Microlevel manufacturing process simulation of carbon fiber/epoxy composites to analyze the effect of chemical and thermal induced residual stresses, *Journal of Composite Materials,* **46**, 2012, pp. 993-1005.

[12] J. Moosburger-Will, M.Greisel and S. Horn, Physical Aging of Partially Crosslinked RTM6 Epoxy Resin, *Journal of Applied Polymer Science*, **131**, 2014, pp. 41121.