THERMOPLASTIC SURFACES FOR JOINING OF THERMOSET CFRP – EFFECT OF CURING CYCLE ON INTERFACIAL BOND STRENGTH

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Abstract

An evaluation of the influence of curing cycles with varying heating rates on interphases between thermoplastic surfaces and thermoset carbon fiber reinforced plastics (CFRP) is presented. Polyetherimide (PEI) films were co-cured with a carbon fiber (CF) reinforced resin system based on tetraglycidyl methylene dianiline (TGMDA) and aromatic hardeners in a vacuum-assisted resin transfer molding (VARTM) process. Dissolution experiments of PEI within a hot stage set-up revealed a strong dependency of the curing cycle and amount of dissolved material. Furthermore, single-lap-shear tests gave evidence that the curing cycle and the dimension of the interphase affects the composite´s performance with an average difference of approximately 82 % in the apparent shear strength of the specimens. The development of the thermoplastic rich interphase, especially the interaction with the fiber architecture, is believed to be the dominant effect in relation to the fracture behavior and overall performance of the composite.

1. Introduction

The application of thermoplastic surfaces on thermoset CFRP offers new possibilities of joining CFRP parts with flexible and efficient processes such as fusion welding or film diffusion welding. Thereby it is possible to overcome the drawbacks (weight, quality management…) of state-of-the-art joining technologies for thermoset CFRP currently used in aerospace industry such as adhesive bonding or the use of mechanical fasteners. However, the interphase between thermoplastic and thermoset is a key element where polymer compatibility and effects of processing have to be considered in more detail.

Some thermoplastics, such as polyethersulfone (PES), polysulfone (PSU) and polyetherimide (PEI) are known to be soluble in the uncured resins and have been used to toughen epoxy resins without decreasing other desirable mechanical properties [1-4]. If such a suitable combination of thermoset and thermoplastic surfacing medium is used, an inter-diffusion of macromolecular chains of both materials takes place. As the epoxy resin cures, a strong interfacial bonding between the thermoplastic and the epoxy is formed by a reaction induced phase separation mechanism [5]. In the case of a thermoplastic surfacing layer, a gradient three-dimensional interphase between the thermoplastic and the epoxy resin develops during curing of the resin. The solubility of the thermoplastic in the epoxy resin system is strongly dependent on temperature and the crosslinking progress of the resin system. Differences in curing conditions can cause diverse material morphologies [6, 7].

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Usually the manufacturer or user of a resin system defines a curing cycle to guarantee the desired properties of the cured resin system. A curing cycle consists of a defined heating and cooling rate, a curing temperature and curing time. Sometimes a curing cycle includes several dwells in dependence of the resin system or the processing technology. However, the temperature profile can vary due to the low thermal conductivity of the resin and the exothermic heat of reaction during crosslinking [8]. Furthermore, the loading of an oven or an autoclave can influences the curing conditions [9]. Therefore, certain tolerances must be accepted within a curing cycle.

Up to date only a few activities focused on gradient interfaces between thermoplastic films and epoxy resins [10-13] and the influence of the curing conditions on gradual interphases have not been addressed in detail.

This study provides information about the effect of differences in the curing cycle on the characteristics of interphases between epoxy resins and thermoplastics. The dissolution, as the first step of interphase formation, of PEI during curing cycles with heating rates from 0.5 K/min up to 5 K/min is determined. The effect of interphase sizes has been evaluated by single-lap shear tests and optical microscopy of composite cross sections. Possible reasons for interphase properties and their consequence on interfacial bond strength are proposed.

2. Materials and Experimental Details

2.1 Materials

Polyehterimide (Ultem 1000, Ajedium Films, Solvay), an amorphous thermoplastic, was selected for the study.

The resin system used for all experiments was an aerospace grade epoxy resin, based on tetraglycidyl methylenedianiline (TGMDA) and aromatic hardeners, for liquid composite molding (LCM) processes. The fiber reinforcement of LCM-manufactured laminates was composed of layers of commercial non-crimped fabrics (NCF), based on (0°/90°) biaxial layers of carbon fibers (HTS 12K).

2.2 Sample Preparation

Composites out of NCF and thermoplastic films for single-lap-shear testing were made in a vacuum-assisted resin transfer molding (VARTM) process. The mold was in each case preconditioned with release agent (Locite 770-NC Frekote), evacuated and heated up to 100 °C. Afterwards the preforms were infused with LCM-resin. Heating to the final cure temperature of 180 °C was realized with different heating rates between 0.5 K/min and 2.6 K/min. The final curing temperature was kept constant for two hours, followed by a slow cooling. Specimens for single-lap-shear tests had a thermoplastic film in the middle layer of the fiber reinforced composite $(0°/90°)_4$-PEI-$(90°/0°)_4$.

2.3 Characterization Techniques

An optical microscope Olympus BX41M equipped with a camera Olympus SC30 was used to analyze cross sections of CFRP specimens. The specimen were polished and etched with dichloromethane (DCM) to remove the PEI fraction. Additionally the microscope was used to observe the dissolution of PEI in the epoxy resin system during different curing cycles. For this purpose, a hot stage Mettler Toledo HS82 with a controller unit HS1 was combined with the microscope. Three strips of PEI film were embedded in a drop of epoxy resin, covered with a glass slide, and placed onto a sample holder.

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The dissolution process was investigated for temperature cycles with different heating ramps between 0.5 K/min and 5 K/min until 180 °C and a subsequent curing at 180 °C for two hours.

Single lap shear tests were performed according to DIN EN 2243-1. The composite specimens had a thickness of approximately 2 mm, a width of 25 mm, and a length of 238 mm. The length of overlap was 12.5 mm. The specimens were tested using a universal testing machine model UPM 250 (Hegewald & Peschke) with a rate of loading of 80 N/s at room temperature. For each composite type at least six specimens were tested.

3. Results and Discussion

3.1 Dissolution experiments

Dissolution experiments have been made within a typical range of heating rates allowed in curing cycles for aerospace epoxy resin systems. The hot stage experiments show a strong dependency of the curing cycle and dissolution progress (Figure 1). PEI starts to dissolve at approximately 120 °C and the width of a PEI film decreases in dependence of the temperature and the state of crosslinking of the resin system. For a cycle with a heating rate of 0.5 K/min the dissolution process stops at approximately 160 °C whereas for a heating rate of 5 K/min the dissolution process lasts until a certain period of time at 180 °C.

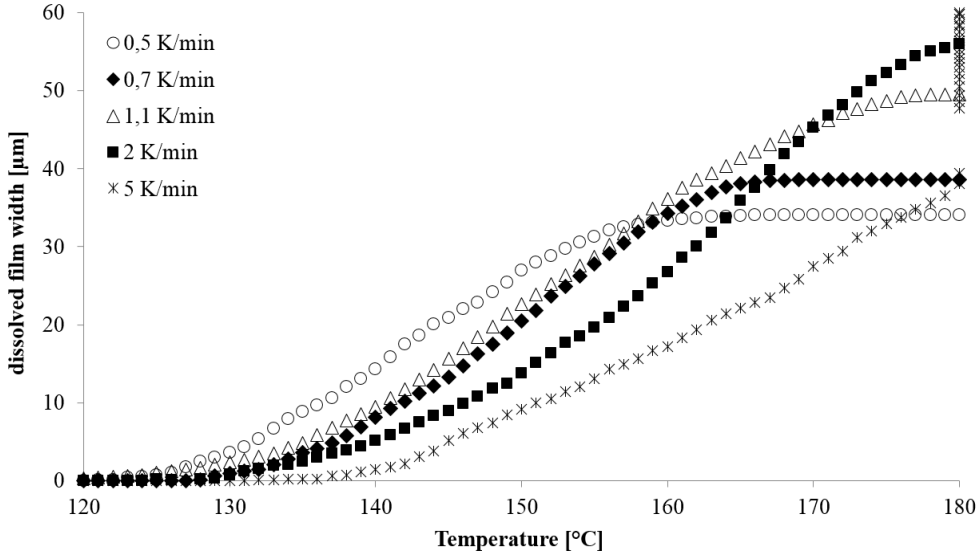

Figure 1. Dissolution of thermoplastic film width during different curing cycles of epoxy resin.

The final amount of dissolved material or dissolved film width is listed in Table 1. It varies between a heating rate of 0.5 K/min and 5 K/min by 76 %. As expected, high temperatures and low degrees of crosslinking are favorable to dissolve a lot of thermoplastic material in the epoxy resin system.

Table 1. Dissolved film width in different curing cycles.

Heating rate	*0.5 K/min*	*0.7 K/min*	*1.1 K/min*	*2 K/min*	*5 K/min*
Dissolved film width	*34.1 µm*	*38.6 µm*	*49.5 µm*	*56.0 µm*	*60.0 µm*

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3.2 Single-lap-shear tests

Single-lap-shear (SLS) tests are a good mean for a comparative evaluation of bonds. The loading conditions are a mixture of shear stress and peel stress, which is typical for bonded aircraft structures. As shown in previous work [14] the joining by means of thermoplastic-thermoset interphases showed good results comparable or even higher than monolithic reference samples. In this study, the influence of heating rates was investigated with samples made with 0.5 K/min, 1.1 K/min and 2.6 K/min, which is the limit of the RTM press used. It has to be mentioned that heating rates higher than 2 K/min only lead to minor differences for the amount of dissolved material (see Table 1).

The shear strength of the various composites measured using the single-lap-shear test method is summarized in Figure 2. All values are normalized to the values of samples made with the lowest heating rate of 0.5 K/min. The shear strength of CFRP joints with thermoplastic films correlates with the amount of dissolved thermoplastic film. The higher the heating rate, the more material is dissolved and the higher is the apparent shear strength.

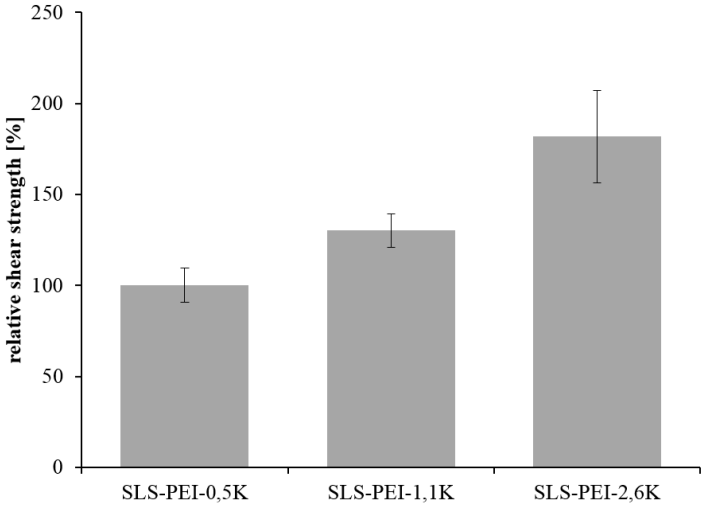

Figure 2. Single-lap shear strength

Fracture surfaces of SLS samples are shown in Figure 3. Specimens manufactured with 0.5 K/min have near the interphase cohesive fractures on both sides of the adherents. In contrast, specimen cured with 2.6 K/min show fracture of the adherent b) and failure in the area of the first fiber plies adjacent to the PEI interlayer.

Figure 3. Fracture surfaces of SLS specimens produced with a heating rate of 0.5 K/min a) and 2.6 K/min b) and c).

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3.3 Microscopy

Etched and polished cross sections of composite specimen (Figure 4) reveal an increasing penetration depth of the interphase in the carbon fibers with rising heating rate. The etched PEI rich interphase is visible as white dots between the carbon fibers on each side of the remaining PEI film in the middle of the specimen. The different fracture behavior of the specimen, shown in the previous section, can be attributed to the interphase dimension. The thermoplastic domains pose as obstacles for cracks and the crack requires additional energy to propagate. The high amount of inherently tough thermoplastic in and adjacent to the joining zone is supposed to rise the resistance of the composite under shear and peel loads.

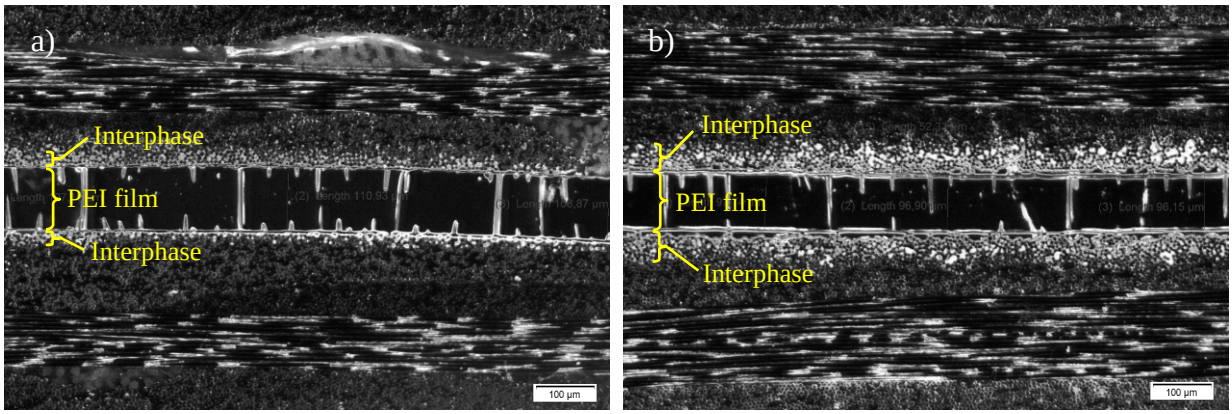

Figure 4. Penetration depth of interphase between carbon fibers in specimens produced with a heating rate of 0.5 K/min a) and 2.6 K/min b).

3. Conclusion

The curing cycle influences the interphase dimension and mechanical performance of a CFRP structure. It could be shown that the heating phase, in a range typical for technologies such as liquid composite molding (LCM) or the autoclave routine, is of major importance for the dissolution step of interphase formation. Almost the whole dissolution reaction takes place during heating. Low heating rates lead to less dissolution of thermoplastic than high heating rates. It is assumed that high temperatures and simultaneously a low degree of crosslinking are favorable to dissolve a lot of thermoplastic material in the epoxy resin system. SLS tests gave evidence that curing cycle and amount of dissolved thermoplastic affects the composite performace with average differences of approximately 82 % in the apparent shear strength of the specimens. Furthermore, the fracture behavior changes from near the interphase cohesive fracture to fracture of the adherent. Cross sections showed growing thermoplastic rich interphase regions for increasing heating rates. The high amount of inherently tough thermoplastic in and adjacent to the joining zone is supposed to affect the resistance of the composite under shear and peel loads positively.

Altogether, the study provides basic information of the characteristics of CFRP components with thermoplastic surfaces for new joining applications. Recommendations for specifications and design criterions can be derived.

Future attempts are directed towards the interaction of the fiber architecture and the development of the interphase structure as well as on the influence of physical and chemical environmental effects. Another key aspect, currently under investigation, is the effect of crosslinking on the final morphology of the interphase and its dependence on the mechanical performance of the composite.

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References

[1] C. B. Bucknall, I. K. Partridge. Phase separation in epoxy resins containing polyethersulphone. *Polymer*, 24: 639-644, 1983

[2] J. H. Hodgkin, G. P. Simon, R. J. Varley. Thermoplastic toughening of epoxy resins: a critical review. *Polymers for Advanced Technologies*, 9: 3-10, 1998

[3] G. Di Pasquale, O. Motta, A. Recca. New high-performance thermoplastic toughened epoxy thermosets. *Polymer*, 38: 4345-4348, 1997

[4] C. Bucknall, A. H. Gilbert. Toughening tetrafunctional epoxy resins using polyetherimide. *Polymer*, 30: 213-217, 1989

[5] R. J. J. Williams, B.A. Rozenberg, J.-P. Pascault. Reaction-induced phase separation in modified thermosetting polymers. *Advances in Polymer Science*, 128: 95-156, 1997

[6] E. Girard-Reydet, V. Vicard, J.-P. Pascault, H. Sautereau. Polyetherimide-modified epoxy networks: influence of cure conditions on morphology and mechanical properties. *Journal of Applied Polymer Science*, 65: 2433-2445, 1997

[7] J. Zhang, Q. Guo, B. L. Fox. Study on thermoplastic-modified multifunctional epoxies: influence of heating rate on cure behaviour and phase separation. *Composites Science and Technology*, 69: 1172-1179, 2009

[8] N. Amdouni, H. Sautereau, J.-F. Gérard, J.-P- Pascault. Epoxy networks based on dicyandiamide: effect of the cure cycle on viscoelastic and mechanical properties. *Polymer*, 31: 1245-1253, 1990

[9] N. Slesinger, T. Shimizu, A. R. A. Arafath, A. Poursartip. Heat transfer coefficient distribution inside an autoclave. *Proceedings of the 17th International Conference on Composite Materials (ICCM 17), Edinburgh, UK*, July 27-31, 2009

[10] M. T. Heitzmann, M. Hou, M. Veidt, L.-J. Vandi, R. Paton. Morphology of an interface between polyetherimide and epoxy prepreg. *Advanced Materials Research*, Vols. 393-395, 184-188, 2012

[11] L.-J. Vandi, M. Hou, M. Veidt, R. Truss, M. T. Heitzmann, R. Paton. Interface diffusion and morphology of aerospace grade epoxy co-cured with thermoplastic polymers. *Proceedings of the 28th International Congress of the Aeronautical Sciences (ICAS), Brisbane, Australia*, September, 2012

[12] B. Lestriez, J.-P- Chapel, J.-F. Gérard. Gradient interphase between reactive epoxy and glassy thermoplastic from dissolution process, reaction kinetics, and phase separation thermodynamics. *Macromolecules*, 34: 1204-1213, 2001

[13] Y.-S. Kim, S.-C. Kim. Properties of polyetherimide/dicyanate semi-interpenetrating polymer network having the morphology spectrum. *Macromolecules*, 32: 2334-2341, 1999

[14] P. Bruckbauer, F. Weiland, U. Beier, K. Drechsler. Characterization of thermoplastic/thermoset combinations – potential application for joining. *Proceedings of the European Conference of the Society for the Advancement of Material and Process Engineering (SAMPE), Amiens, France*, September 15-17, 2015

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