INFLUENCE OF CURING DEGREE ON THE MECHANICAL PERFORMANCE OF POLYMER MATRIX COMPOSITES

M. Wolfahrt[1], G. Pilz[2] and R.W. Lang[3]

[1]Polymer Competence Center Leoben GmbH, Roseggerstraße 12, 8700 Leoben, Austria
Email: markus.wolfahrt@pccl.at, Web Page: http://www.pccl.at
[2]Department Polymer Engineering and Science, Chair of Material Science and Testing of Polymers, Montanuniversität Leoben, Otto Glöckel-Str. 2, 8700 Leoben, Austria
Email: gerald.pilz@unileoben.ac.at, Web Page: http://www. kunststofftechnik.at
[3]Institute of Polymeric Materials and Testing, Johannes Kepler University Linz, Altenbergerstr. 69, 4040 Linz, Austria
Email: Reinhold.Lang@jku.at, Web Page: http://www.jku.at/ipmt

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Abstract
As a continuation of our previous work, which concerned the relationship between curing degree and key neat resin properties, an experimental study was carried out to evaluate the applicability and limitations of the results of the characteristic neat resin properties on polymer matrix composites. The glass transition temperature, storage modulus and fracture energy of a unidirectional carbon fiber-reinforced epoxy laminate were studied as a function of the degree of cure. Using dynamic mechanical and fracture mechanics tests a good correlation between the key neat resin and laminate properties was established.

1. Introduction

Although advanced polymer-matrix composites have been successfully applied as construction materials for lightweight structures, there is still a need to economise the processing cycles by reducing resin cure temperature and time [1]. As the latter parameters directly affect the degree of cure and thus the composite performance profile considerable research has been conducted to clarify the complexities of the degree of cure on the neat resin properties [2-4]. These include storage modulus as a function of temperature, glass transition temperature and fracture energy [5-7]. For the dry material state it was found that the glass transition temperature increased continuously to its maximum value for the fully cured material. On the other hand, a decrease of the storage modulus values were determined with increasing degree of cure within the same curing range. The fracture energy, however, showed a value increase up to a curing degree of about 83%. At higher curing degrees, the fracture energy values levelled off. As expected, wet specimen conditioning led to lower glass transition temperature as well as storage modulus values. Simultaneously, the fracture energy plateau increased for the wet material state.

In this study, cure temperature and time were again changed systematically to investigate its influence on the corresponding laminate properties. A commercially availible carbon fiber reinforced prepreg was impregnated with the same 180 °C degree cure epoxy resin formulation as used for the experimental work at the neat resin level. Based on dynamic mechanical as well as fracture mechanical measurements on laminate specimens an attempt is made to establish a correlation between relevant neat resin and composite properties.

2. Experimental

2.1. Materials and laminate fabrication

The compression molding process was used to produce quasi-unidirectional (UD) woven fabric laminates (6 plies; 3 mm laminate thickness) consisting of a standard modulus carbon fiber T700 and a non-stoichiometric epoxy resin formulation. A few glass fibers were inserted in the weft direction to make the unbalanced prepreg integrity during handling [8]. The polymer matrix was the same as described in [2], so the reader is referred to this article for sample preparation and descriptions. By having applied the appropriate curing parameters regarding temperature and time (Table 1), it was possible to produce laminate plates with the same degree of cure as for neat resins. The fiber volume content in the cured laminate plates was calculated as specified in [9] to 50±3 %. Somewhat higher fiber volume content (about 57 Vol%) was determined for one laminate plate cured to 96 %.

Table 1. Cure programs for various degree of cure of carbon-fiber/epoxy laminates.

Degree of cure (%)	Cure program (temperature/time)
80	95 °C/1 h + 140 °C/1 h
90	95° C/1 h + 150 °C/1 h
94	95° C/1 h + 170 °C/3 h
96	95° C/1 h + 200° C/3 h

2.2 Test methods

As the complete experimental set up for the determination of the key neat resin properties is given in [2], the focus in this section is laid on the experimental procedure for the characterization of the carbon fiber/epoxy specimens. All dynamic mechanical tests were carried out according to ISO 6721-5 [10] using rectangular specimens in the dimension 80x10 mm. Two measurements were performed for each cure program. The thermo-mechanical storage modulus as a function of temperature was measured with a Mettler-Toledo DMA861e (Fa. Mettler-Toledo, Schwerzenbach, CH) applying three-point bending for each cure condition. Measurements were performed in a temperature range from 10 °C to 275 °C at a heating rate of 2 °C/min and a test frequency of 1 Hz. It should be noted that both force and displacement were adjusted with respect to fiber reinforcement, ensuring that the material deformation was done within the linear viscoelastic region.

Mode I fracture toughness testing was carried out on a servo-hydraulic test machine (MTS 858, MTS Systems Corporation, Berlin, Germany). Double cantilever beam (DCB) specimens (155 x 20 mm) were loaded continuously with a constant crosshead-rate of 10 mm/min until the crack was approximately 100 mm in length. A thin polymer film (length of 50 mm) was placed in the bondline during specimen manufacturing for crack initiation. Load introduction was done via steel loading blocks that were bonded to the outer surface of the DCB specimen using a two-component epoxy adhesive. Fracture mechanic tests were done in laboratory air (23 °C, 50 % relative humidity) and at least five samples were tested for each cure program. All measurements were conducted on dried specimens (dry conditions: storage of specimens in an oven at 70 °C for 24 hours).

3. Results

In Fig. 1 the glass transition temperature, T^f_g, (onset-value) is plotted as a function of the degree of cure for both neat epoxy and carbon fiber-reinforced specimens. In good agreement with the results

observed at the neat resin level, a significant increase in Tg with increasing degree of cure was determined for the composite material. The effect of reinforcement on the glass transition temperature leads, as expected, to consistently higher values compared to the neat resin. However, this is not true for a curing degree of 96 %. The T_g value is lower, which can be attributed to the higher fiber volume content (57 Vol%) in the specimens.

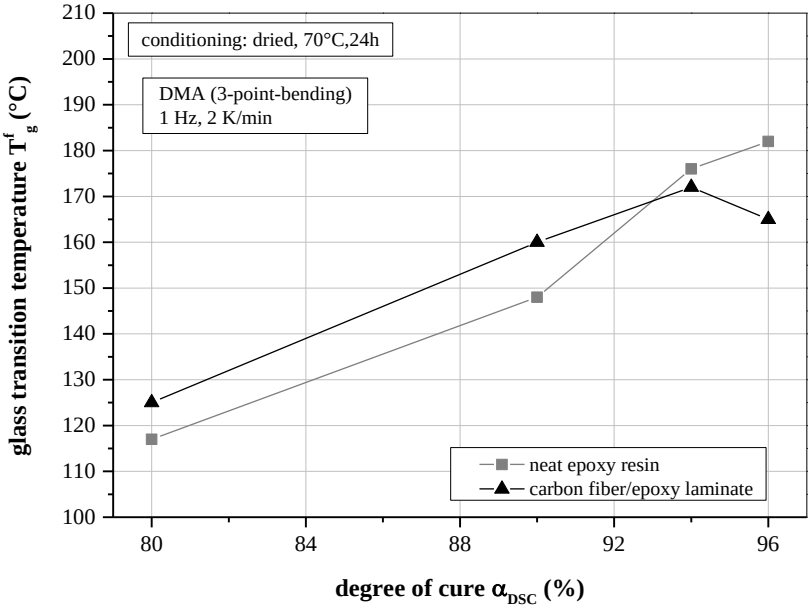

Figure 1. Comparison of onset glass transition temperature obtained from DMA measurements and the degree of cure for neat epoxy and carbon fiber/epoxy specimens (dry condition).

The storage modulus values at 23°C, $E'_f(23)$, for both neat and carbon fiber-reinforced specimens obtained from DMA measurements are shown in Figure 2. The laminate values were normalized to a fiber volume content of 52% using the equations as recommended in [9]. It can be seen, that with increasing degree of cure the storage modulus will tendentially decrease. These results are in accordance with investigations published by other authors [11-13]. Their studies have shown that the lower modulus at room temperature of the more crosslinked network is a consequence of the lower density. Our results from density measurements on neat resin samples confirm these conclusions. However, due to the reinforcing fibers this behavior is less pronounced for the composite storage modulus values.

A direct comparison of the fracture energy, G_{IC}, of both neat and carbon fiber-reinforced specimens on the degree of cure is depicted in Fig. 3. The results clearly indicate, that the laminate G_{IC} values, first, increase with increasing degree of cure. After a curing degree of 91% and under consideration of the calculated standard deviations the interlaminar G_{IC} values levelled off at 0.27 kJ/m² (mean value). On the other hand the neat resin fracture energy remains roughly constant on the same level (mean value of 0.16 kJ/m2). An explanation of the higher laminate G_{IC} values can be made in terms of a larger crack tip damage zone in combination with possible effects associated with the fiber/matrix interface (see e.g. [14]).

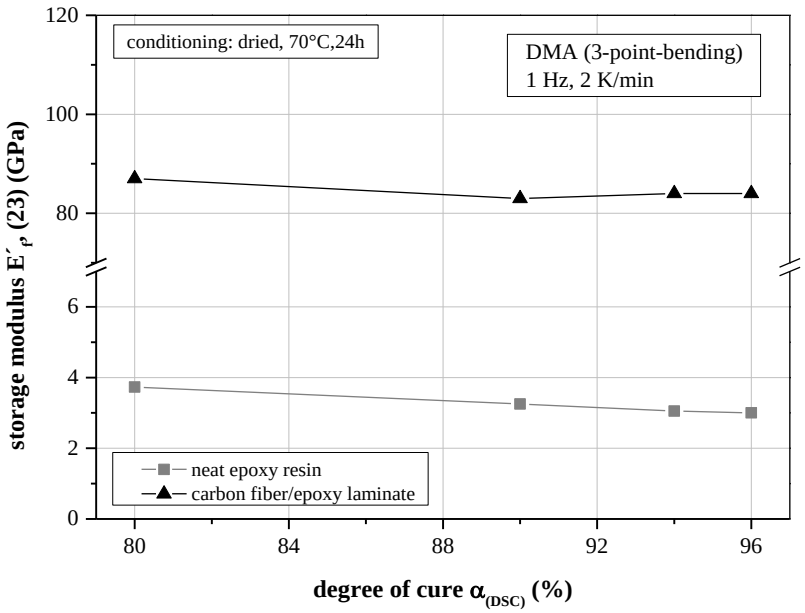

Figure 2. Comparison of storage modulus at 23°C obtained from DMA measurements and the degree of cure for neat epoxy and carbon fiber/epoxy specimens (dry condition).

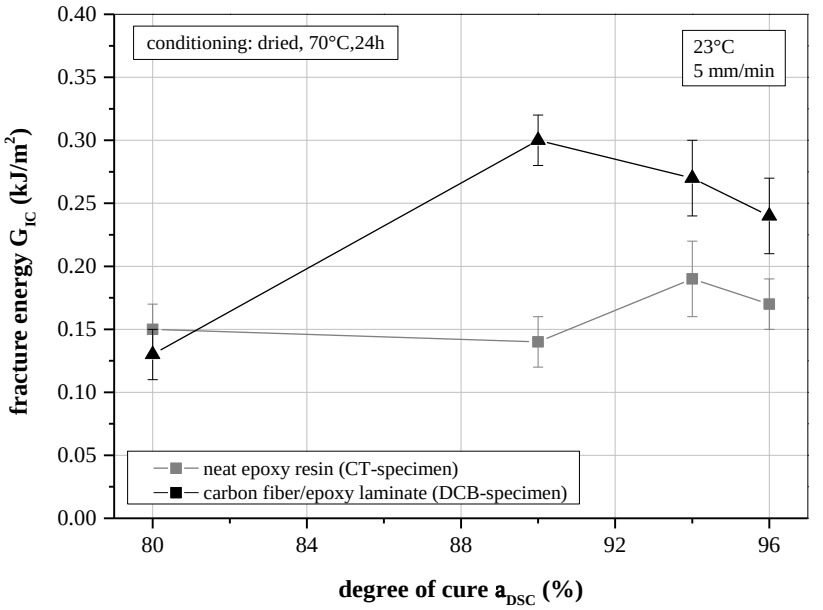

Figure 3. Comparison of fracture energy values and the degree of cure for neat epoxy and carbon fiber/epoxy specimens (dry condition).

4. Conclusions

Based on a series of experiments in which cure temperature and time were systematically varied, it was possible to characterize the influence of the degree of cure on glass transition temperature storage modulus and fracture energy. For a given fiber type, good correlations between characteristic neat resin and the corresponding laminate properties have been shown to exist. Hence, the developed test

methodology is basically suitable for carrying out an effective material characterization of neat resin formulations for high performance composite applications applying structure-property relations (neat resin level vs. laminate level). Moreover the tests on neat resins offer considerable advantages in terms of a lower effort for specimen preparation and testing.

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References

[1] R. Hardis. Cure kinetics characterization and monitoring of an epoxy resin for thick composite structures. PhD thesis, Iowa State University, United States, 2012.

[2] M. Wolfahrt, G. Pilz, R.W. Lang, R. Eugen, W. Krumlacher and A.K. Plessing. Influence of the curing degree on key resin properties of high Tg epoxy resins for composites. *Proceedings of the 27th International Conference SAMPE Europe, Paris, France*, 2006.

[3] M. Wolfahrt, G. Pilz and R.W. Lang. Einfluss des Aushärtegrades auf wesentliche Werkstoffeigenschaften eines Epoxidharz-Matrixwerkstoffes. *Proceedings of the 15th Symposium Verbundwerkstoffe und Werkstoffverbunde, Kassel, Germany*, 2015.

[4] M. Wolfahrt. Characterization of epoxy resin formulations for composites - Influence of curing degree and curing path. PhD thesis, Institute for Material Science and Testing of Polymers, Montanuniversitaet Leoben, Leoben, Austria, 2009.

[5] R.W. Lang, H. Tesch and G. Schornick. 125°C-curable epoxies - A systematic approach to new resin formulations for composites. *Proceedings of the 8th International Conference of the Society for the Advancement of Materials and Processing Engineering European Chapter, Amsterdam, Netherlands*, 1987.

[6] R.W. Lang, G. Herrmann and K. Schneider. Material development and second source qualification of carbon fiber/epoxy prepregs for primary and secondary airbus structures. *Proceedings of the 35th International SAMPE Symposium and Exhibition: Advanced Materials, Anaheim, United States*, 1990.

[7] R.W. Lang, H. Tesch, A. Robert, A. Neu and K. Schneider. A new approach towards the assurance of product quality of prepregs for structural applications *Proceedings of the 11th International European Chapter Conference SAMPE, Basel, Switzerland*, 1990.

[8] B. Wang, K. Maekawa, N. Uda, K. Ono and H. Nagai. Compressive failure analysis of quasi-isotropic composite laminates fabricated with quasi-unidirectional woven fabric. *Journal of Composite Materials*, 50:231-241, 2016.

[9] MIL-HDBK-CMH-17-1G. *Composite Materials Handbook, Volume 1, Polymer Matrix Composites, Guidelines for Characterization of Structural Materials*, SAE International, 2012.

[10] ISO 6721-5 „Plastics - Determination of Dynamic Mechanical Properties - Part 5: Flexural vibrations - Non-resonance Method". International Organization for Standardization, Genf, Switzerland, 1996.

[11] J.B. Enns and J.K. Gillham. Effect of the extent of cure on modulus, glass transition, water absorption, and density of an amine-cured epoxy. *Journal of Applied Polymer Science* 28:2831-2846, 1983.

[12] B.-G. Min, J.H. Hodgkin and Z.H. Stachurski. The dependence of fracture properties on cure temperature in a DGEBA/DDS epoxy system. *Journal of Applied Polymer Science*, 48:1303-1312, 1993.

[13] V. B. Gupta and C. Brahatheeswaran. Moleculare packing and free volume in crosslinked epoxy networks. *Polymer, 32*:1875-1884, 1991.

[14] P.A. Smith, *Polymer Matrix Composites*, (R. Talreja and J.-A.E Månson, ed.), Elsevier, 2001.