Use of DMA in the Development of Resins for Cryogenic Tank Applications

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Introduction

The storage of hydrogen in cryogenic tanks requires materials that can withstand extremely low temperatures. Carbon fiber-reinforced polymer (CFRP) composites with epoxy resins as the matrix material are a promising solution for meeting the lightweight requirements of the aerospace and automotive industries. Dynamic mechanical thermal analysis (DMA) is an indispensable tool for the optimal development of these materials. This application note explains how DMA is used to evaluate and optimize epoxy resin formulations for cryogenic applications and presents the results of a recent dissertation at the Polymer Engineering Institute of the University of Bayreuth (https://www.polymer-engineering.de/) which is dedicated to this topic. (https://www.polymer-engineering.de/).

Methods and Materials

Dynamic Mechanical Thermal Analysis (DMA) was used to measure the viscoelastic properties of resin formulations over a wide temperature range down to low temperatures. The following viscoelastic parameters were recorded::

- Storage modulus (E'): A measure of the material's elastic stiffness.
- Loss modulus (E"): A measure of the energy loss due to internal friction and damping.
- Tan δ: The ratio of the loss modulus to the storage modulus, a measure of the material's damping properties.
- Glass transition temperature (T_g/T_α): The temperature range in which the material fully transiitons from a glass-like to a rubber-like state.
- The sub-glass transition temperatures, T_β and T_γ: Temperature ranges in which individual sections of the polmyer network change their mobility and transition from energy-elastic to viscoplastic behavior at low temperatures.

All measurements were carried out with a NETZSCH DMA *Eplexor*® 500 N in a temperature range from -140°C to 300°C.

Epoxy resins used:

- **EP1:** Standard epoxy resin, based on diglycidyl ether of bisphenol A (DGEBA) with polyetheramine (PEA) as hardener. This combination serves as a reference material without any additional modifications.
- **EP2:** DGEBA resin with dicyandiamide hardener (DICY) with urea accelerator.
- **EP3:** DGEBA resin with isophorondiamine (IPDA) as the cold hardener, which is also typically used in the manufacture of rotor blades.
- **EP4:** DGEBA resin with 4,4' diaminodiphenylsulphone (DDS) hardener for high-temperature resins in the aerospace industry.
- **EP5**: Epoxy resin, based on tetraglycidylmethylendianillin (TGMDA) with DDS hardener with higher crosslinking density.
- **EP2X:** Modified version of EP2 with portions of core shell particles for modifying toughness at low temperatures.

Overview of the DMA Analysis Results

Glass Transition Temperature (T_g)
The glass transition temperature (T_g) is a critical point that defines the application limits of a material as a decrease in the storage modulus and a maximum in the loss modulus or tan d. Epoxy resins with a higher degree of cross-linking have a higher T_g, which means that they retain their stiffness at higher temperatures.

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Storage Modulus (E')

The storage modulus increases with decreasing temperature (figure 1). At -196°C, the resins tested showed a significantly higher storage modulus, indicating increased stiffness. This property is important because when the modulus of the matrix changes, the behavior is expected to be significantly different from that at room temperature. This is a critical parameter in the design of tank structures.

Loss Modulus (E") and Damping Factor tan δ

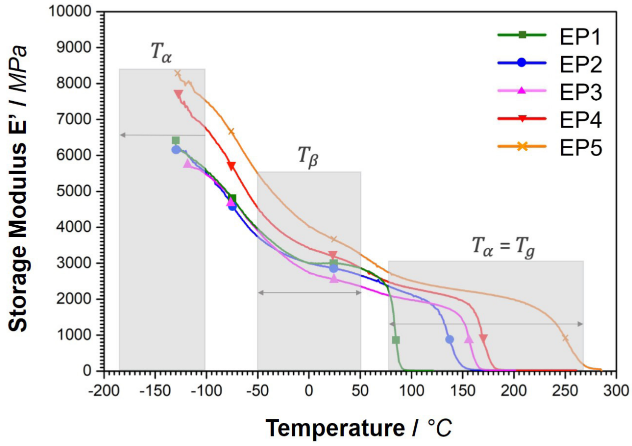
The loss modulus, which indicates the damping properties of the material, decreases at cryogenic temperatures. This indicates that the material dissipates less energy through internal friction at cryogenic temperatures, resulting in a more brittle characteristic. The DMA results were consistent with the fracture toughness tests at -196°C – the material becomes increasingly brittle at low temperatures and becomes increasingly linearly elastic with loss of plastic deformability (figure 2).

Influence of the Toughness Modification

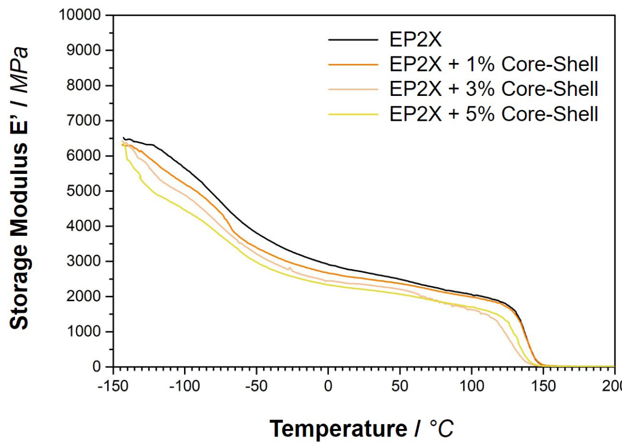
The addition of toughness-modifying additives, such as nanoscale core-shell particles, improved the fracture toughness of the resins without compromising much on the required stiffness of the fiber-plastic composite at elevated temperatures. This results in a balanced combination of stiffness and toughness, which is ideal for cryogenic tanks under varying temperature loads. It can be seen that the modified resins have a lower E' value at -196°C. This means that these materials do not become as brittle and a kind of 'residual ductility' remains, which is important for the balance between structural integrity and increased fracture toughness of the cryogenic tanks for micro-crack resistance.

The addition of silicone nanoparticles results in softening of the network, which is indicated by a lower modulus than that of the unmodified EP2 over the entire temperature range. At low temperatures in particular, plasticization of the network can be seen via the glass transition temperature of the silicone core. The modulus is lower at all temperatures because silicone has a significantly lower stiffness than pure epoxy. The chemical compatibility between silicone and epoxy is improved by the thermoplastic shell, which causes the modulus to reduce less sharply.

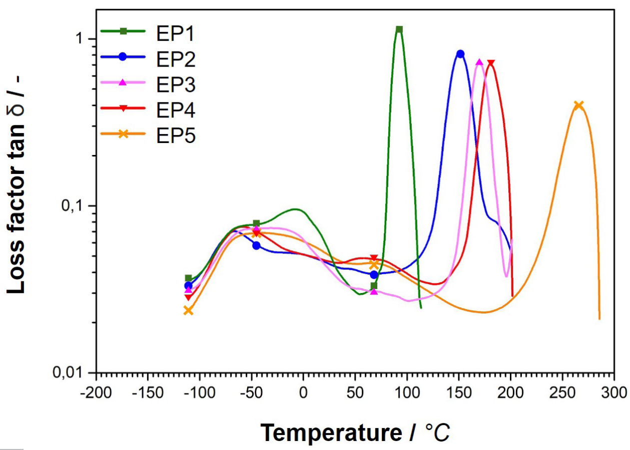
The T_g is slightly reduced as softening of the network starts earlier at 5% addition (figure 3). However, after the maximum loss factor tan d, the T_g only drops to +142.9°C. The actual softening point of the material, defined by the drop in E' modulus, is +122°C. However,



1 Storage modulus E'of all samples (EP1 to EP5) as a function of temperature from DMA *Eplexor*® 500 measurements with transition temperature including T_g.



2 Loss factor tan δ as a function of temperature of EP1 to EP5.



3 Comparison of storage modulus for modified and unmodified resins.

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this is high enough for EP2X to ensure adequate safety of the composite at external temperature requirements of up to +90°C. The component stiffness up to +122°C is relevant for the assembly of bonded joints or attachments to the tank structure, as these need to be dimensionally stable at a curing temperature of, for example, +120°C, since they need to be reheated locally in order to make bonded joints for attachments or repairs.

Correlation with the Mechanical Behavior of Crogenic Tanks at -196°C

The thermo-mechanical properties determined by DMA correlate directly with the mechanical behavior of the CFRP material that can be used for cryogenic tank structures.

- The increased molecular stiffness at low temperatures results in higher tensile strength, but simultaneously to reduced elongation at break, making the material more brittle.
- Therefore, material design for cryogenic tanks must be more conservative, taking lower strain levels into account.
- Rsistance to crack propagation: Modified epoxy resins with toughening additives show improved crack toughness and reduced risk of microcracking.

The Use of DMA in Material Development for Cryogenic Tank Applications

- Material selection and modification: DMA helps select the best resin formulations that provide an optimum combination of modulus and toughness. This is particularly important for ensuring the structural integrity and safety of cryogenic tanks.
- Process optimization: By analyzing the glass transition temperature and rheological properties, it is possible to optimize the curing conditions and processing temperatures to achieve the best mechanical properties.
- Quality assurance: Regular DMA testing during the production of materials and components ensures that the materials have consistent properties and meet the stringent requirements for cryogenic applications.
- Long-term stability: Long-term studies and repeated temperature cycles in the DMA provide insight into the long-term stability and reliability of materials under cryogenic conditions. This is critical to the safety and longevity of cryogenic tanks.

Conclusion

Dynamic mechanical thermal analysis (DMA), or also called dynamic mechanical thermal analaysis (DMTA), is an essential tool in the development of materials for cryogenic applications. It allows detailed evaluation of the thermo-mechanical properties of epoxy resins and their optimization for use in carbon fiber-reinforced cryogenic tanks. Through systematic use of DMA, materials can be developed that can withstand the extreme requirements and offer high performance and safety. More detailed information can be found in Dr Hübner's thesis:
Modifizierte Epoxidharzformulierungen zur Herstellung von kohlenstofffaserverstärkten kryogenen Wasserstoffspeichern im automatisierten Legeverfahren - EPub Bayreuth (uni-bayreuth.de)

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