Polyurethane prepregs – A new concept for CFRP processing

A new polyurethane-based prepreg pairs the excellent mechanics of polyurethane matrices with the easy handling of prepregs. Outstanding mechanical properties, efficient and highly automated processing together with fast curing cycles – all combined into a single system.

The use of pre-impregnated fibres, or prepregs, has gained a lot of importance in the production of composite materials over the last couple of years. This can be attributed to their advantageous handling properties.

When using a prepreg, a composite part can be manufactured out of one single component compared to the individual handling of fibre and (usually two) resin components. This drastically reduces error sources in the application. Additionally, when using a prepreg, no liquid resin travels through the fibre layers during the infusion or impregnation phase, which causes much less fibre displacement. Thus, the mechanical quality of a prepreg-based composite is often higher than comparable RTM or wet-pressed parts.

However, prepreg technology is not suitable for all applications. Especially, prepregs appear less suitable when it comes to highly automatized processing with fast cycle times.

Another important downside is the kinetics of the system. Since all the reactive components are mixed together in the prepreg matrix, the curing process proceeds inevitably after establishing...
the B-stage. According to Arrhenius’ law, a formulation curing at 120°C in several minutes reacts at room temperature in several days. So most prepregs are either not stable when stored at room temperature and must be stored at -18°C, or offer unsatisfactory long curing times at elevated temperatures.

The PU-based solution

With Evonik’s polyurethane-based prepreg system, both issues can be solved (Figure 1). Polyurethanes are becoming more and more important in the composite industry. They offer fast curing cycles combined with very good mechanical properties, not to mention the excellent toughness of PU-based composites over epoxy systems. But being highly reactive, and thus fast curing, makes these systems unsuitable for prepreg systems, where a certain latency is needed to ensure storage stability.

Evonik’s PU prepregs based on aliphatic diisocyanates Vestanat® IPDI offer the required latency due to the use of reversibly blocked isocyanates via blocking-agent-free uretdione chemistry. Aliphatic isocyanates can be transferred into stable dimers (uretdiones, Figure 2); the back reaction into the isocyanate usually starts at temperatures around 180°C. This temperature can be lowered to about 120°C by the use of suitable catalysts.

An uretdione of a diisocyanate has four isocyanate groups in total. Two of them are blocked in the uretdione ring, while two isocyanate groups remain free. When formulating this uretdione with a stoichiometric amount of polyol component to react all four isocyanate groups, the overall reaction to the cured polyurethane takes place in two well-separated steps: the free isocyanate groups instantly react to polyurethane chains with blocked isocyanate groups inside. This resembles the pre-polymer or the B-stage. The second step can only occur if the remaining isocyanate groups in the uretdione rings are unblocked – which happens only at temperatures above 120°C.

The result is a prepreg which is truly storage stable at room temperature and still offers fast curing at elevated temperatures.

However, the rate-limiting step for the curing process is not the polyurethane formation but rather the ring opening reaction. This leads to curing times of about 30 minutes at 140°C or 2 minutes at 190°C. These times are strongly related to the amount of catalyst added in the formulation – as does the storage stability. The fully catalyzed prepreg is stable for about 10 weeks at room temperature and even 4 weeks at 40°C. Formulations with less catalyst cure significantly slower (30 minutes at 180°C) but have significantly improved storage stability of over 2 years at room temperature.

Suitable for automation...

The unique combination of fast curing cycles with improved storage stability is not the only thing setting Evonik’s PU prepregs apart. Another important property with significant influence on the composite manufacturing process is that the B-stage pre-polymer is solid at room temperature. This causes the prepreg to be relatively form-stable and non-tacky. Together with a relatively low Tg of ~50°C, this offers a variety of processing options for the PU prepreg. By heating it moderately to 60-80°C, the system becomes drapeable and tacky, and thus can be handled like any other prepreg, especially since the curing reaction will not kick in at these temperatures. This is important for hand lay-up processes, which can take several hours. For automated production of composites, this means the prepreg can be formed thermoplastically at moderate temperatures. Only in the final curing step is the thermoset formed. So the prepreg can ideally be used for preforming steps without the need for additional binders and return to the original solid, form-stable and non-tacky state after cooling down (Fig. 3, left); drastically easing automated handling, i.e. with robots. So in comparison with RTM processing, which is often used in the automotive industry for large-volume applications, PU prepregs hold two major processing advantages. First, the fabric does not need any additional binder to be pre-formed. This saves one processing step in the production chain and the saved binder does not influence the matrix system, may it be in wetting the fibres or in the curing reaction itself. The second major advantage is that the infusion process itself is no longer required. This is even more important since this saves time in the actual RTM press. Since the curing reaction is comparably faster than state-
of-the-art epoxy RTM systems, the overall curing cycle is shortened by the infusion time.

**... and exterior applications**

In addition to the processing properties, the system also offers very promising composite properties. This holds for exterior applications with high demands on surface properties as well as for structural parts with high mechanical stress.

In exterior applications of composites, the production of Class-A surfaces is one of the main issues to be solved. Evonik’s PU prepreg might be a solution for these surfaces with matrix shrinkage values as low as 0.9%. Comparable epoxy resins often exceed 4% shrinkage. Also, the PU prepreg is solely based on aliphatic isocyanates. This means that, depending on the polyol formulation used, we can formulate UV-stable resins which drastically exceed the weather stability of aromatic systems as they are common today for epoxy and PU formulations alike (Figure 4).

For structural parts, it is obviously more the classical mechanical values which are of interest. In classical fibre-dominated properties such as tensile strength and compression strength, the PU prepreg performs comparably to state-of-the-art high-tech epoxy formulations. But concerning matrix-dominated values such as ductility, the material has significant advantages. For the neat resin, this is represented in a modulus of elasticity of 3500 MPa, a K1C of 1.7 MN/m3/2 and an elongation at break of 8% – values that exceed comparable epoxy resins by 30-50% (Figure 5).

This high ductility can also be found in the values for the composite – in this case reinforced with 300 g/m² ±45° NCF carbon. The shear strength (103 kJ/m²) and the shear modulus (5200 kJ/m²) are significantly higher than in epoxy-based systems. So this clearly helps balancing the downsides of the anisotropic behaviour of composite materials to a certain extent. This is especially beneficial where stress and load situations occur which are not along the fibre orientation – i.e. impact scenarios, may it be small stone chipping or larger crashes.

**Conclusion**

In conclusion, Evonik’s new polyurethane prepreg advantages are twofold: On one hand, it has very good overall properties with very high ductility combined with superior surface properties. On the other hand, it offers a completely new way of processing semi-finished goods. Binders are no longer needed and infusion is not required; resulting in a shorter overall cycle time. Moreover, this PU Prepreg is storage stable (for about 10 weeks at room temperature).

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