

Keeps Its Cool

Study of the Resistance of Glass-Fiber-Reinforced Polyamides to Coolants

Applications under the hood in the automotive industry are characterized by strong temperature fluctuations and involve various media, such as coolants. Although metals are highly capable of coping with these conditions, engineering plastics find them challenging. An enhanced measurement methodology has been developed for the early detection of damage resulting from contact between coolant and glass-fiber-reinforced polyamide 66.

Polyamide 66 (PA66) is a popular material for technical applications, with even the unmodified raw material boasting very good performance characteristics. But polyamides are increasingly being pushed to their performance limits by a combination of relentless tightening of the thermal, mechanical and chemical requirements imposed on components on one hand and a simultaneous desire to save on weight and costs on the other. To ensure that these limits are not exceeded

and that components will not fail, parts made from polyamides have to meet stringent requirements that are laid down in various international and company-specific regulations.

The various regulations usually differ in detail only, and fail to adequately reproduce real world scenarios. The test environments, measurement methods and property limits laid down in standards tend to be empirical and are rarely justified scientifically.

Not even established classes of polymer can escape from the trend of launching ever-higher-performance products onto the market and the unremitting tightening of the requirements imposed on materials. The knock-on effect is that glass-fiber-reinforced PA66, too, must be continually modified and optimized. While there is development potential in the areas of polymer synthesis, glass fiber sizing, and application-specific additives, major or revolutionary improvements in properties are not to be expected for this system of materials and so nuances in materials development and downstream processing are coming increasingly to the fore. If synergistic effects are to be achieved between the individual components, a holistic assessment of the materials system is needed, because the properties or modes of action of individual components cannot be used to draw inferences about the system as a whole. It is precisely in this interaction that the greatest development potential lies. Success requires collaboration by various partners along the value chain, each of which have their own interests at heart. The Institut für Kunststofftechnik (IKT, Institute of Polymer Technology) at the University of Stuttgart, Germany, working with strategic industry partners, has developed a methodology for measuring the influence of coolant on glass-fiber-reinforced PA66.

Long-Term Effects of Coolants and their Conditions

When it comes to materials intended specifically for use in coolant-carrying components, the properties of the materials



The fracture surface of a 4 mm specimen of glass-fiber-reinforced polyamide 66 with a longitudinal crack (© IKT)

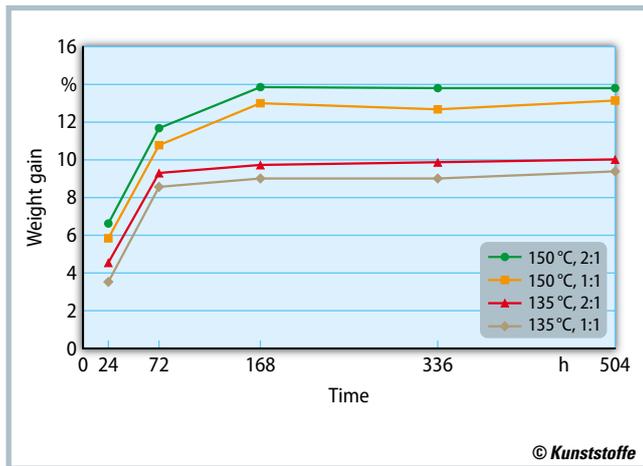


Fig. 1. Percentage weight gain of a 4 mm thick test specimen subjected to different conditioning regimes in coolant-water mixtures (source: IKT)

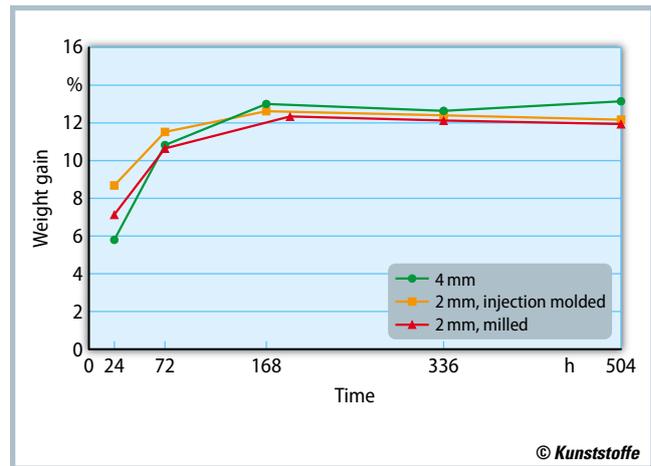


Fig. 2. Percentage weight gain of different specimens during conditioning at 150°C in a coolant mixture (1:1) (source: IKT)

in their dry initial state are not critical to their selection or optimization. Much more important are their long-term properties under alternating external conditions. Due to this happenstance, development projects in this area always take a great deal of time.

The current state of the art is to condition test specimens of sometimes different shapes and sizes in coolant in a sealed pressure vessel. The specimens are completely wetted with the coolant mixture and conditioned at the autogenous temperature-dependent vapor pressure.

The most common coolant resistance tests are carried out at constant temperatures of 108°C to 135°C for periods ranging from 504h to 3000h. The coolants are usually mixed with water in a ratio of 1:1.

However, these tests bear very little resemblance to reality. What is needed is tests on coolant-carrying components that are tailored to the intended application. The coolant only comes in contact with the interior of a component. The temperature on the exterior is totally different. Similarly, the properties can be influenced by contaminants, such as lubricating oils or fuels. Such tests could conceivably consist in wetting one side with coolant or exposing it to coolant flow and subjecting the other side to attack by atmospheric oxygen. A further point to consider is that the cooling circuit is a dynamic system involving heating and cooling of the coolant at certain rates, and changing temperature gradients and pressures [1].

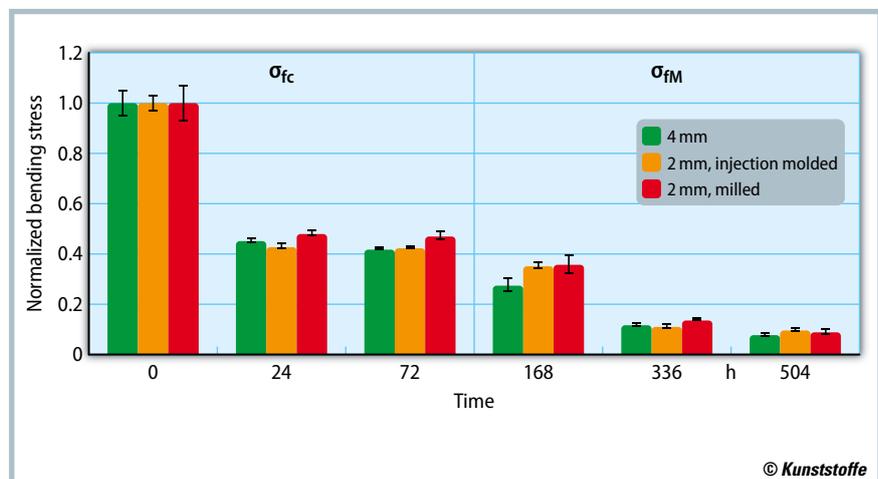


Fig. 3. Normalized bending stress of conditioned specimens at 150°C in a coolant mixture (2:1) as a function of conditioning time (source: IKT)

Component Damage due to Solvolysis

Long-term tests involving alternating loads and cooling/heating cycles could provide a clearer insight into the continuous use of glass-fiber-reinforced PA66 as a material for coolant-carrying components. However, on closer examination, the design of such tests becomes quite complicated and must pass the cost-benefit analyses of the quality assurance departments operated by large companies which place an emphasis on practicality and cost-efficiency. In addition, the comparability of the results suffers from the fact that different companies impose different requirements on the coolant-carrying components and that these also vary with the class of vehicle in which they are used. Trying to quantify the damage caused by one-sided conditioning also imposes enormous demands on the test

methods, which are mostly mechanical by nature [2].

It is difficult to predict in any great detail the chemical interaction between the coolant and the glass-fiber-reinforced PA66. Coolant consists of many components whose interactions with each other and their environment are highly complex. As products of polycondensation, polyamides are susceptible to hydrolysis. Once the moisture content is exceeded in the equilibrium state, covalent bonds will undergo hydrolysis again if water is present and the temperature is right. Similarly, alcoholysis may occur, with the ethylene glycol contained in the coolant causing molecular degradation. Material properties are always affected by molecular degradation. Although this can be counteracted with tailored additives, it can only be delayed and not prevented over the long term [3].

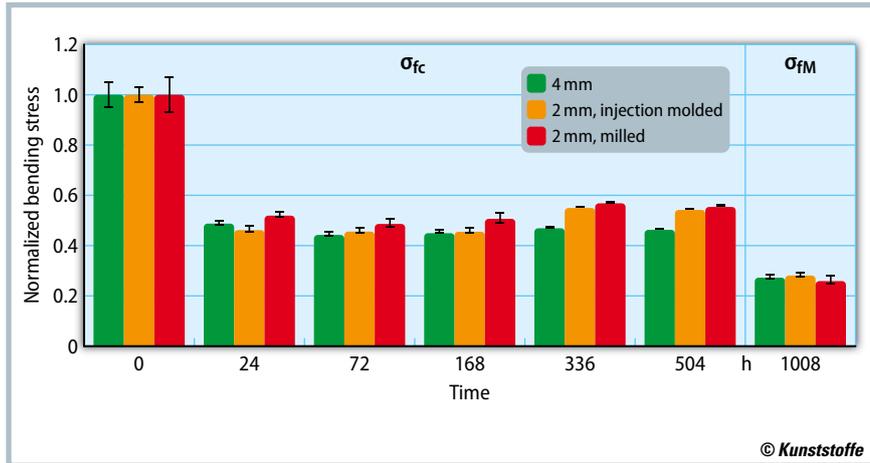


Fig. 4. Normalized bending stress of conditioned specimens at 135°C in a coolant mixture (1:1) as a function of conditioning time (source: IKT)

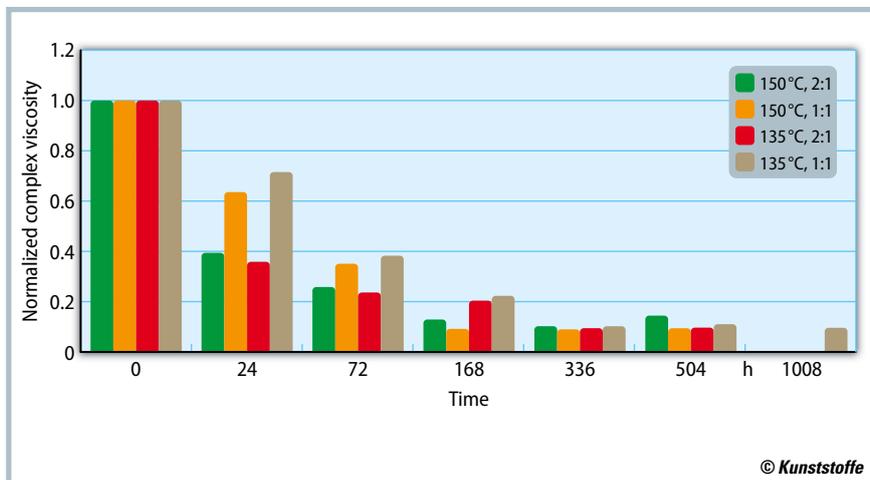


Fig. 5. Normalized complex viscosity of the 2 mm, injection molded test specimens for various conditioning regimes (source: IKT)

and may lead to micro-cracking. This leads to a change in diffusion behavior of the conditioning medium, and that impacts the damage done to the material.

The amount of coolant absorbed during conditioning is a function of temperature and time, and is additionally determined by specimen thickness, specimen preparation and the concentration ratio of the coolant. This is illustrated in **Figure 1** for a 4 mm thick specimen conditioned at two different temperatures (135°C and 150°C) as well as in two different coolant concentrations (coolant-water mixture in the ratios 1:1 and 2:1). The higher the conditioning temperature, the more media is absorbed. The weight gain for a 2:1 coolant concentration is also measurably greater than for a ratio of 1:1. The differently prepared specimens tend to absorb coolant at different rates at the start of conditioning. But the saturation level, established after a certain time, is comparable (**Fig. 2**).

Early Insights through Rheometry

While the mechanical properties of the conditioned specimens, after having changed dramatically from the outset of conditioning, undergo only moderate change as a function of the chosen conditioning regime, rheological measurements are capable of detecting a measurable change in the material itself at an early stage. The dramatic initial change that occurs in the mechanical tests is due to the plasticizing effect of the coolant and not to any instantaneous damage, as the specimens are tested immediately after conditioning and without being dried. For the rheological measurements, the conditioned specimens must be dried, because otherwise solvolytic degradation while the measurement was being performed would affect the validity of the results. For this, an oscillating rotary rheometer in a plate-plate arrangement is used. If the flow behavior of the polymer changes as a function of conditioning, it can be concluded that the material has suffered damage. Although no direct cor-

Test Specimen Treatment and Varying Conditioning Regimes

Specimens used for conditioning tests are typically 4 mm thick, yet this is not usually the dimension of the actual component (**Title figure**). For the most realistic test, specimens would need to be machined directly from the relevant components, where possible. The problem is that machining prior to media conditioning has great potential for the results to be misinterpreted. Machining damages the surface, alters the ratio of the core/edge layer, exposes fibers on the surface

	4 mm	2 mm, injection molded	2 mm, milled
Bending stress	113°C	110°C	108°C
Complex viscosity	80°C	69°C	40°C

Table 1. Continuous service temperatures of different specimen geometries for the coolant mixture in the ratio 1:1 (source: IKT)

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References & Digital Version

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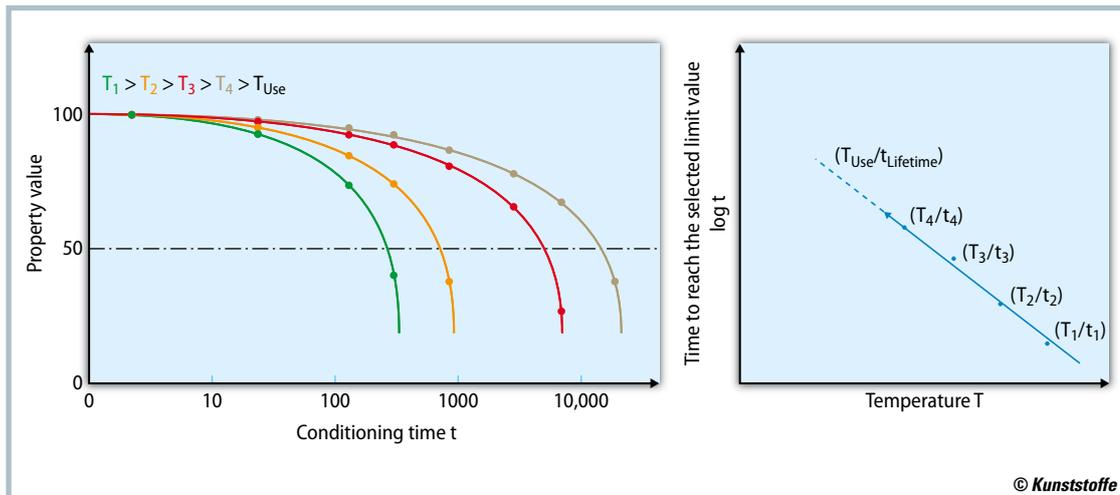


Fig. 6. Lifetime prediction according to DIN EN ISO 2578 [5] (source: IKT)

relation exists between the rheometric and mechanical characteristics, if one type of material is treated with different additives or if different glass fiber sizes are used, it is possible to draw conclusions about their mode of action in respect of coolant resistance. Similarly, different specimen geometries or preparatory treatment yield different results. Thus, a material change triggered by conditioning in coolant can be detected with the aid of the complex viscosity. Such a statement is possible because the zero shear viscosity η_0 is related via a constant K to the molecular weight M_w as follows:

$$\eta_0 = K \cdot M_w^{3,4}$$

Figure 3 shows how conditioning in a 2:1 coolant mixture at 150°C influences the bending stress, normalized to the dry initial state, for various specimens. A change occurs after just 168h due to a solvolytic degradation. In comparison, it takes more than 500 hours' conditioning at 135°C in a 1:1 coolant mixture before a measurable change is produced (**Fig. 4**).

On the other hand, a change in the complex viscosity, normalized to the initial state, yields a substantial change after just

24h (**Fig. 5**). A higher conditioning temperature and higher coolant concentration have a measurably greater effect on the complex viscosity than do more moderate conditions. Only after a conditioning period of more than 336 hours is the material so damaged by the chosen conditioning conditions that there is no longer any discernible difference between the different specimen geometries.

If the measurement results are used to perform a lifetime prediction according to DIN EN ISO 2578 (**Fig. 6**), the difference between the various specimen preparation methods becomes readily apparent [4]. Thicker test specimens have a higher continuous service temperature than thinner test specimens. Injection molded specimens also show a higher continuous service temperature than machined test specimens.

Conclusion

Aside from conventional tests of the various mechanical properties of conditioned specimens at defined sampling periods, rheological measurements constitute a promising method of detecting material changes. Studies on conditioned

test specimens are able to provide very early detection of material changes, allowing storage capacity to be run down and costs to be saved.

In addition, rheological measurements are much more sensitive than the mechanical tests to variations in conditioning medium composition on the polymer, and the number of test specimens needed is low. Different specimen geometries can be compared without the need to adjust the experimental setup, e.g. in the determination of mechanical properties. Rheological measurements are thus a rugged test method which, through correlation with mechanical characteristics, are highly informative as regards material suitability, especially as they can also identify differences in specimen preparation.

This composite view of material changes allows the IKT to shorten development times for material recipes and to evaluate various conditioning regimes and specimen dimensions. However, if broad acceptance within the industry is to be obtained, further studies should look at striking a balance between proven company-specific regulations and academic solutions. ■

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