

Time Temperature Dependence of Long Fiber Reinforced Polypropylene Manufactured by Direct Long Fiber Thermoplastic Process

K. A. Weidenmann, M. Grigo, B. Brylka, P. Elsner, T. Böhlke

Abstract—In order to reduce fuel consumption, the weight of automobiles has to be reduced. Fiber reinforced polymers offer the potential to reach this aim because of their high stiffness to weight ratio. Additionally, the use of fiber reinforced polymers in automotive applications has to allow for an economic large-scale production. In this regard, long fiber reinforced thermoplastics made by direct processing offer both mechanical performance and processability in injection moulding and compression moulding. The work presented in this contribution deals with long glass fiber reinforced polypropylene directly processed in compression moulding (D-LFT). For the use in automotive applications both the temperature and the time dependency of the materials properties have to be investigated to fulfill performance requirements during crash or the demands of service temperatures ranging from $-40\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$. To consider both the influence of temperature and time, quasistatic tensile tests have been carried out at different temperatures. These tests have been complemented by high speed tensile tests at different strain rates. As expected, the increase in strain rate results in an increase of the elastic modulus which correlates to an increase of the stiffness with decreasing service temperature. The results are in good accordance with results determined by dynamic mechanical analysis within the range of 0.1 to 100 Hz. The experimental results from different testing methods were grouped and interpreted by using different time temperature shift approaches. In this regard, Williams-Landel-Ferry and Arrhenius approach based on kinetics have been used. As the theoretical shift factor follows an arctan function, an empirical approach was also taken into consideration. It could be shown that this approach describes best the time and temperature superposition for glass fiber reinforced polypropylene manufactured by D-LFT processing.

Keywords—Composite, long fiber reinforced thermoplastics, mechanical properties, dynamic mechanical analysis, time temperature superposition.

I. INTRODUCTION

ONE of the principal aims in automobile technology is the reduction of the weight of vehicles in order to minimize fuel consumption but to retain comfort and safety. To reduce

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development costs, modeling of the mechanical properties under near-service loads is necessary to overcome the need of elaborate experimental tests. Long glass fiber reinforced thermoplastics (LFT) represents a promising material system for the structural use in automotive components allowing at the same time for a large-scale manufacturing in both injection or compression moulding processes [1]. Garnier [2] gives a comparison of this processing route to conventional routes and underlines the benefit of the direct processing route regarding the fiber length in the manufactured parts. Usually, starting point for the manufacturing process is the use of long-fiber reinforced pellets. Alternatively, the direct processing starting from pure polymer pellets and continuous fibers has been developed a decade ago based on an in-line compounding (D-LFT/ILC-process) [3]. Tröster [4] describes the relevant mechanical properties of polypropylene fabricated by such a D-LFT/ILC process. Unfortunately, the time and temperature dependency of the material system has not been investigated at that time.

Polymers and polymer matrix composites show similar properties when temperature is elevated but strain rate is lowered in a specific manner. This time-temperature superposition (TTS) can be observed in time domain experiments like relaxation test and uniaxial tension test or in frequency domain experiments like the Dynamic Mechanical Analysis (DMA) measurements. For polymers and polymer based composites, many investigations have been done in relaxation mode. For long-fiber reinforced polypropylene, Chevali et al. recently published results on the time-temperature-stress superposition [5]. In contrary to the results presented here, the LFT materials were based on pellets. Nevertheless, it was shown that the description of the TTS for long-fiber reinforced PP following WLF- and Arrhenius approaches is feasible. Hereby, the shift function a_t correlates the dependence of the relaxation modulus at different relaxation times and temperatures to extrapolate the time dependence for a reference temperature T_0 .

$$R(t, T) = R(t_0, T_0) \quad (1)$$

This correlation can be described by (2):

$$\ln a_t = \ln \frac{t}{t_0} = f(T, T_0) \quad (2)$$

According to this definition the strain rate and temperature dependence of the stiffness in uniaxial tension tests will be defined by the following shift function a_ε , which defines the correlation of the secant modulus E_s to the strain rate $\dot{\varepsilon}$ and temperature T .

$$E_s(\dot{\varepsilon}, T) = E_s(\dot{\varepsilon}_0, T_0) \quad (3)$$

In frequency domain experiments based on a DMA, the stiffness response of the material under cyclic loading can be described with the storage modulus E' . For a constant angular rate ω with an sinusoidal stress loading $\sigma(t) = \sigma_0 \sin(\omega t)$ by an stress amplitude σ_0 and an strain response $\varepsilon(t) = \varepsilon_0 \sin(\omega t + \delta)$ with the strain amplitude ε_0 and the offset angle δ , the storage modulus can be defined as

$$E' = \sigma_0 / \varepsilon_0 \cos(\delta) \quad (4)$$

This definition is also true, if the mean stresses are taken into consideration. Therefore, a third shift function a_ω has to be defined which correlates the storage modulus at different angular rates and temperatures

$$E'(f, T) = E'(f_0, T_0) \quad (5)$$

The necessary time temperature shift a_T can be described by different approaches. Many authors state (e.g. [6]) that this superposition is based on the molecular behavior and is therefore related to the activation energy. Therefore, equations formulated based on the activation energy, such as the Arrhenius equation, are regarded to be adequate for the description of the TTS. Besides Arrhenius' approach, the approach presented by Williams, Landel, and Ferry (WLF) is also based on reaction kinetics [7]. Alternatively, several empirical approaches also show good agreement with testing results.

The shift factor $\ln a_T$ is described by Arrhenius via following equation, where k is a quotient form activation energy U and the ideal gas constant R .

$$\ln a_T = \ln t/t_0 = -k \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (6)$$

WLF used the principle of free volume by Eyring to describe polymers 50 K above the glass transition temperature [7].

$$\lg a_T = \lg t/t_0 = \left(\frac{-c_1(T-T_0)}{c_2 + (T-T_0)} \right) \quad (7)$$

For a frequency-temperature sweep, (7) can be expressed as presented in (8).

$$\lg a_T = \lg f_0/f = \left(\frac{-c_1(T-T_0)}{c_2 + (T-T_0)} \right) \quad (8)$$

As the theoretical shift factor follows an arctan function, the following approach by Keuerleber [8] was also used by the authors to describe the TTS of long-fiber reinforced PP based on the stiffness shift due to different strain rates and different frequencies, respectively.

$$\ln a_T = -a \cdot \arctan[b(T-T_0)] \quad (9)$$

In contrary to Arrhenius and WLF, this approach has been derived empirically and has no physical background.

DMA's were carried out by Brylka et al. [9] to assess the influence of flow orientation on the dynamic mechanical behaviour of D-LFT. It was found that the temperature-dependent mechanical behaviour is also depending on the flow orientation in the process. Nevertheless, a validation of the presented master curves, i.e. a correlation with quasistatic and dynamic experiments on bulk samples has not been carried out. In this contribution, the investigations are therefore carried out on macroscopic samples for tensile tests at different strain rate levels and different temperatures to be correlated with DMA measurements. This corresponds to the comparison of non-destructive DMA and destructive tensile tests.

II. EXPERIMENTAL

A. Manufacturing of Sample Material

The long glass fiber reinforced thermoplastics direct technology (D-LFT) combined with the in-line compounding of the matrix polymer (D-LFT/ILC) allows compounding the matrix polymer with various additives. As shown in Fig. 1, first the additives are compounded with the matrix polymer in the inline compounding extruder. The modified matrix is then compounded with the glass fibers in the mixing extruder. There are two possibilities to insert the fibers. First, the fibers can be precut. Second, direct fiber feeding is possible. For the investigations presented here, fibers were precut to a length of 20 mm. At the end of the mixing extruder a die creates a molten charge (LFT strand). The LFT strand is then immediately transferred to the compression press holding a suitable mould in which the LFT strand is compression molded at a pressure of 200 bar. During the compression molding, the molten LFT strand flows to fill the cavity, and after cooling the final component can be demolded.

The flow of the LFT material leads to a fiber orientation and thereby to anisotropic properties. Hence, it is possible with the LFT-D/ILC technology to adjust the materials composition to fulfil individual demands of the products [10]. In this work, polypropylene (Copolymer C711-70RNA from DOW), reinforced with 30 w.-% glass fibers (JM473A from Johns Manville) was investigated. The fiber diameter and the resulting average fiber length in the final part are about 14 μm and 12 mm, respectively. For detailed process description it is

referred to [4]. The mould cavity featured a size of 400 x 400 mm².

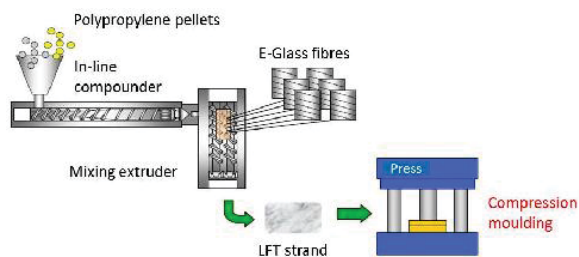


Fig. 1 Process scheme of the long glass fiber reinforced thermoplastics direct technology combined with the in-line compounding of the matrix polymer (D-LFT/ILC process)

B. Sample Geometries

Samples were taken out from the resulting sheets within regions, where the material flow resulted in a profound orientation of the fibers. All specimens were oriented 0° (parallel) to the direction of the material flow.

For the DMAs, prismatic samples with a size of 80 x 10 mm³ were used, the specimen geometry for the tensile tests were dog bone-shaped with a gauge area of 150 x 20 mm². High-speed tensile tests were carried out on samples according to Fig. 2. For all tests, the specimen thickness was set to 3 mm, which corresponds to the thickness of the fabricated sheets.

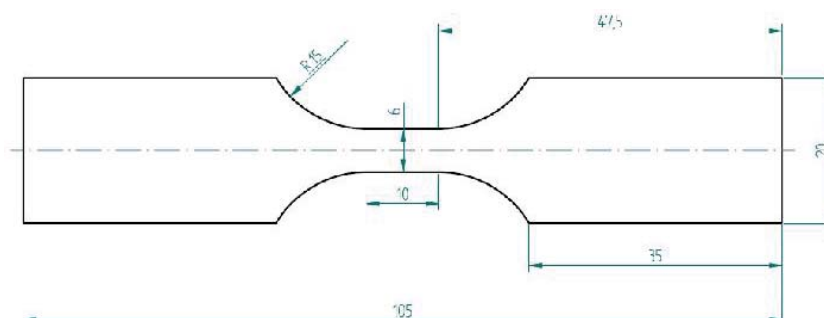


Fig. 2 Specimen geometry for high speed tensile tests

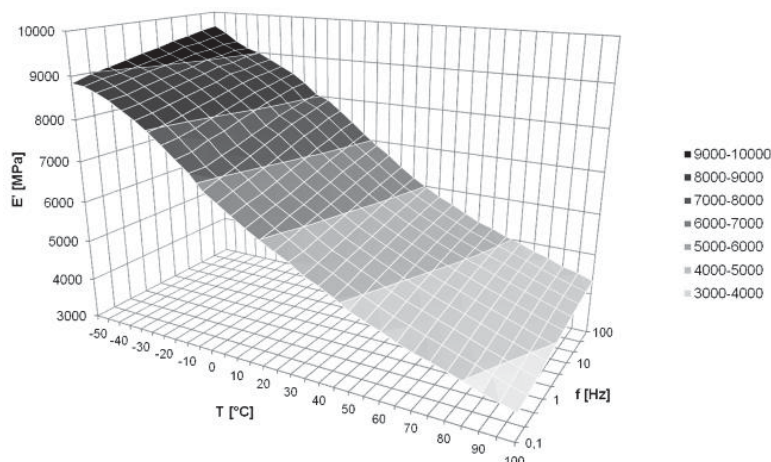


Fig. 3 Storage modulus in temperature-frequency space

C. Testing Procedures

DMA was done in tension mode on a GABO Eplexor 500N with a load cell capacity of 1500 N. The temperature and frequency range for the temperature-frequency-sweep has been -50 °C to 100 °C in 5 °C steps and 0.1 Hz to 100 Hz with three steps per decade. The loads have been defined as strains with a preload of 0.1% by an amplitude of 0.05%.

Quasistatic tensile tests were done on electromechanical universal testing machine from Zwick by using a load cell with a maximum capacity of 10 kN. The samples were heated

with a heating/cooling chamber operated with hot air and a nitrogen cooling, respectively. Strain measurement was done by means of a clip gauge built for elevated and reduced temperatures. The strain rate was set to 0.005 s⁻¹.

High speed tensile tests were done on a servo hydraulic system Zwick 5020 with a haul-off speed between 1 and 10 m/s. Deflection was measured by tracking two lines with a high speed CCD camera with a frequency of 50 kHz.

Quasistatic and high-speed tensile tests were carried out on ten samples each. For the DMA, preliminary tests at room

temperature were carried out first to derive the scatter of the characteristics.

III. RESULTS

The storage modulus in 0° specimen orientation is shown in Fig. 3 in the temperature frequency space.

As expected, the storage modulus E' decreases with decreasing frequency and increasing temperature. In comparison to the storage modulus at room temperature, the increase between room temperature and -50°C is 40% which corresponds to a likewise reduction of 40% from room temperature to 100°C . The stiffness over frequency is given in Fig. 4.

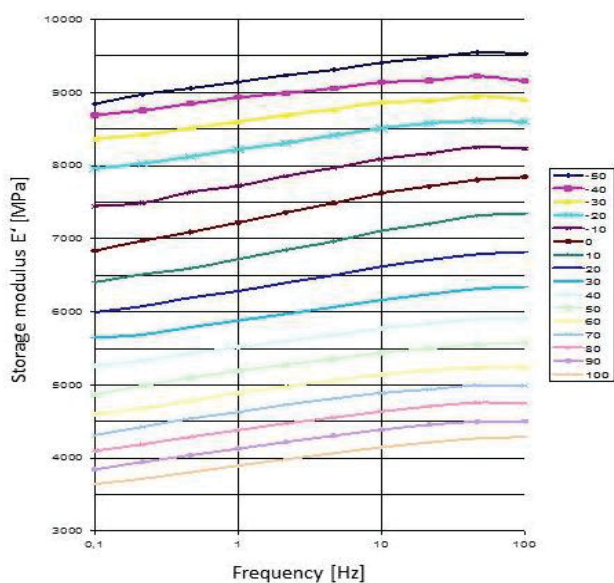


Fig. 4 Storage modulus in temperature-frequency space

Stiffness over frequency at different temperatures is given in Fig. 4. There is a range from 3600 MPa at 100°C and a frequency of 0.1 Hz and 9500 MPa at -50°C and a frequency of 100 Hz.

These results were based on the DMA. In contrary, the experimental results presented in Table I were derived from destructive tensile tests at different strain rates and temperature.

TABLE I
YOUNG'S MODULUS FROM TENSILE TESTING AT DIFFERENT TEMPERATURES AND STRAIN RATES

temperature	0.005 s^{-1}	5 s^{-1}	50 s^{-1}	250 s^{-1}
-40°C	7.5 GPa			
20°C	6.0 GPa	6.0 GPa	7.0 GPa	8.5 GPa
80°C	3.5 GPa			

IV. DISCUSSION

The results given in Table I and those derived from the DMA were interpreted by using different time temperature shift approaches following (6)-(8). For this, results from the

tests under thermal and strain rate influence were grouped. The approaches connect different tests leading to the same or similar result. In this case, Young's modulus was discussed, and two groups were built. For example, a stiffness of 7 GPa can be arrived with a temperature drop of 60 K (from 20°C to -40°C) at a quasistatic strain rate of 0.005 s^{-1} or at room temperature with an increase of the strain rate to 50 s^{-1} , which is 4 decades higher in comparison to 0.005 s^{-1} .

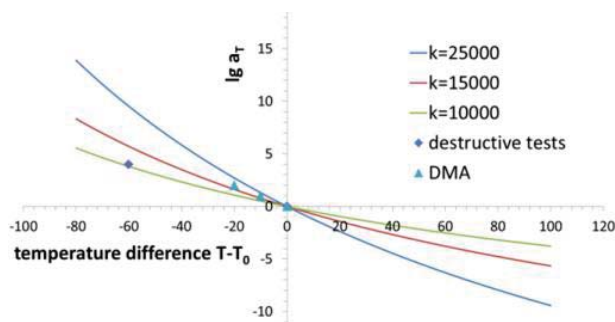


Fig. 5 Arrhenius plot for different values of k (cf. (6)) in comparison to results from destructive and non-destructive DMA tests

From Fig. 5, it is clearly visible that the Arrhenius approach does not allow for fitting both experimental data with the same value of the fit parameter k , which is $k = 15000$ for the DMA measurements and $k = 10000$ for the results from destructive testing. From the DMA measurements, the mastercurve displayed in Fig. 6 can be derived. Following (7), the WLF parameters from this curve can be determined as $c_1 = 24$ and $c_2 = 175$. When this set of WLF parameters is used to plot the experimental data, it is obvious that the WLF approach again is not able to describe both the results from DMA and quasistatic and high-speed tensile tests. This plot is displayed in Fig. 7.

Obviously, both the WLF and the Arrhenius plot does either fit the experimental data derived from DMA tests or the quasistatic and high-speed tensile tests. In contrary, the empirically derived model published by [8] allows for a reasonable fit of all the experimental results. With $a = 4.5$ and $b = 0.04$, the resulting fit based on (9) is shown in Fig. 8.

Firstly, this may be due to the different sample sizes and a resulting difference in the impact of the fiber length as the DMA samples featuring a width of 10 mm which is in the range of the fiber length as it is true for the quasistatic tensile tests having a gauge width of 20 mm. For the high-speed tensile tests, the gauge width had to be reduced to 6 mm as prior to this change, the fracture of the sample did not occur within the gauge length. Nevertheless, the comparison between DMA measurements at 100 Hz and 0.1 Hz and the macroscopic experiments at room temperature show a perfect match as presented in Fig. 9.

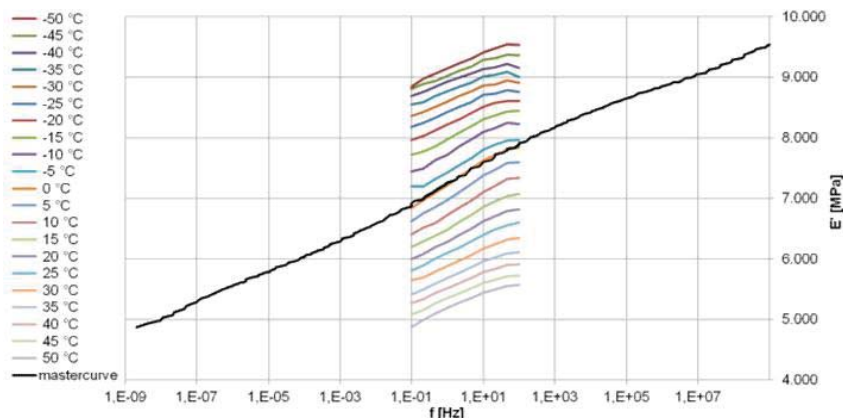
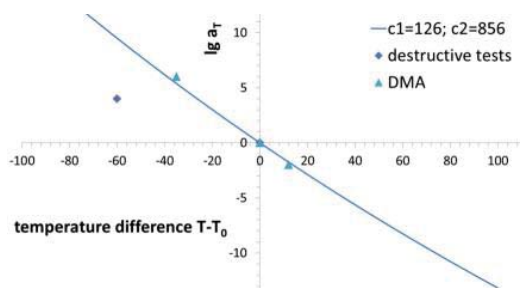
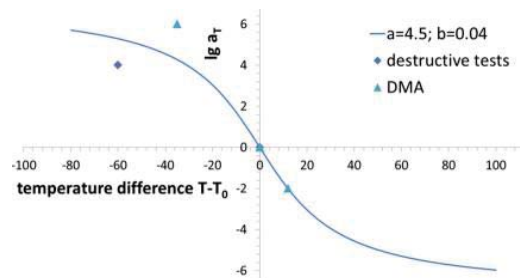
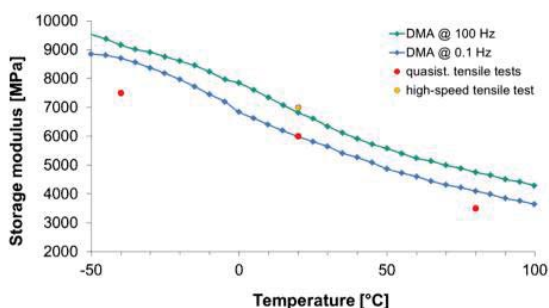
Fig. 6 Master curve derived from DMA tests for $T_0 = 0^\circ\text{C}$ Fig. 7 WLF plot for $c_1 = 126$ and $c_2 = 856$ (derived from the masterplot of the DMA experiments displayed in Fig. 6 and following (8) in comparison to results from destructive and non-destructive DMA testsFig. 8 ARCTAN-plot for $a = 4.5$ and $b = 0.04$ following (9) in comparison to results from destructive and non-destructive DMA tests

Fig. 9 Comparison of storage moduli derived from DMA at different frequencies with those determined from quasistatic and high-speed tensile tests.

Here, it is clearly visible, that the Young's modulus determined at -40°C may be too low. If the Young's modulus would be closer to the DMA curve at 0.1 Hz (which corresponds to the strain rate of the quasistatic experiments), the results of DMA and quasistatic experiments would match perfectly.

V. CONCLUSION

The TTS for polypropylene manufactured in a D-LFT/ILC process was investigated. With an arctan-approach, it is possible to describe the shift factor within the application-relevant temperature range.

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REFERENCES

- [1] M. Schemme, "LFT-development status and perspectives." *Reinforced Plastics*, vol. 52, no. 1, pp. 32-39, 2008.
- [2] M. Garnier, "In-line compounding and molding of long-fiber reinforced thermoplastics (D-LFT): Insight into a rapid growing technology." In: *ANTEC conference proceedings*. Society of Plastics Engineers, 2004, pp. 3500-3503.
- [3] W. Krause, O. Geiger, F. Henning, P. Eyerer, "Development of a Technology for Large Scale Production of Continuous Fiber Reinforced Thermoplastic Composites". *ANTEC conference proceedings*. Society of Plastics Engineers, 2005. pp. 2782-2786.
- [4] S. Tröster, *Materialentwicklung und -charakterisierung für thermoplastische Faserverbundwerkstoffe im Direktverfahren*. Stuttgart University, Germany: Ph.D. thesis, 2003.
- [5] V.S. Chevali, D. R. Dean, and G. M. Janowski. "Flexural creep behavior of discontinuous thermoplastic composites: Non-linear viscoelastic modeling and time-temperature-stress superposition." *Composites Part A*, vol. 40 no. 6, pp. 870-877, 2009.
- [6] J.J. Aklonis, W.J. MacKnight, "Introduction to Polymer Viscoelasticity" New York, CA: John Wiley & Sons, 1983.

- [7] J.D. Ferry, “*Viscoelastic properties of polymers*”. New York, CA: John Wiley & Sons, 1993.
- [8] M. Keuerleber, *Bestimmung des Elastizitätsmoduls von Kunststoffen bei hohen Dehnraten am Beispiel von PP*. Stuttgart University, Germany: Ph.D. thesis, 2006.
- [9] B. Brylka, T. Böhlke, F. Henning, J. Wood, “Anisotrope viskoelastische und temperaturabhängige Eigenschaften langfaserverstärkter Thermoplaste” in *Proc. of the 19th Symposium Verbundwerkstoffe und Werkstoffverbunde*, pp. 634-639, 2013.
- [10] F. Henning, O. Geiger, R. Brüssel, H. Ernst, W. Krause, „LFTs for automotive applications”, *Reinforced Plastics*, vol. 49, no. 2, pp. 24-33, 2005.