TEMPERATURE-DEPENDENT LAP SHEAR STRENGTH OF ADHESIVELY BONDED HIGH-TEMPERATURE RESISTANT THERMOPLASTICS

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ABSTRACT

Due to the development of high-temperature resistant thermoplastics, e.g. polyetheretherketone, these plastics have become more attractive for several applications which require good mechanical properties at high service temperatures. In addition to conventional production processes, adhesive bonding is more and more used to build assemblies with a mix of materials to achieve certain product properties. These products are exposed to high temperatures during their product life, driving the need for a thorough understanding of the substrates, adhesives and their bonds. In order to investigate the temperature-dependent behaviour of the mechanical properties of high-temperature resistant joints, different thermoplastics were analysed in shear tension tests. In these tests three substrates (polyetheretherketone, polyetherimide, and polyamide) and two adhesives (one- and two-component epoxy resin) were tested. The tests were performed at four testing temperatures equally spaced between 20 °C and 200 °C to analyse the temperature-dependent material properties. The specimens were built up as a single-lap joint with a constant adhesive thickness. After curing at definite conditions the adhesively bonded joints were tested in a shear tension test. The results of this test are the lap shear strength and failure patterns. The results were correlated with thermal and mechanical properties of substrates and adhesives, e.g. glass transition temperature and Young's modulus. The experimental analysis reveals a distinct temperature-dependent behaviour of the lap shear strength and failure patterns within the temperature range examined. In general, the lap shear strength decreases with rising testing temperature. Moreover, the failure patterns change from substrate failure to adhesive and cohesive failure of the examined adhesives with rising testing temperature. This implies a significant demand for high-temperature resistant adhesives in the future which can exhibit improved mechanical properties at high temperatures to guarantee an excellent joint between the substrate materials.

IIW-Thesaurus keywords: Adhesive bonding; Lap joints; Shear strength; Thermoplastics.

1 Introduction

Modern designs are subjected to evolving challenges in functionality, resource efficiency and sustainable use of natural resources. Especially under these conditions polymers present new options due to their low weight and efficient processing. Polymer applications benefit from their good material properties as well as using as little energy and material as possible. The development of high performance polymers leads to new applications where formerly metal-based materials were used. Based on the high material costs of these high-performance polymers, hybrid designs become more and more attractive. Here, these materials are combined with low priced standard polymers. Technical difficulties arise in the joining technology of these materials which require a reliable junction under challenging working conditions and thermal loading, with outstanding flexibility in the engineering and processing of these joints. These requirements are especially well fulfilled by adhesive bonding. Advantages and challenges of this bonding technology can be demonstrated e.g. by the adhesive bonding of polyetheretherketone (PEEK). The high resistance to environmental conditions (thermal resistance, ultraviolet resistance etc.) of PEEK is accompanied by a low surface tension [1]. This limits the wettability of PEEK by adhesives. High adhesive strength can only be reached by a pre-treatment of the bonding surface [2]. This can be achieved by various process technologies which either increase the surface area itself, e.g. by etching or roughening, or by activating the surfaces. The most effective and industrially approved process for activating the polymer surface uses plasma technology. Further, adhesives based on epoxy resins (one- and two- component adhesives) with PEEK as adherent were analysed under thermal loading at temperatures up to 150 °C [3-6]. The bondline strength in these studies was sufficient.

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2 Experimental

Within this experimental study three substrates were analysed: polyetheretherketone (PEEK), polyetheremide (PEI) and polyamide 66 (PA66). The PEEK substrates were prepared from flat specimens in the dimensions 210 × 20 × 3 mm. The PEI substrates were produced by splitting tensile test specimens according to ASTM D638-08. The polyamide 66 substrates were cut from injection moulded plates which were manufactured at the KTP. For the adhesive bonding two different epoxy adhesives were examined: a one-component epoxy resin (A1) and a two-component epoxy resin (A2). The one-component epoxy resin cures at temperatures above 140 °C. The curing of the two-component epoxy resin starts immediately after mixing, under ambient conditions.

The geometry of the specimens is shown in Table 1. In this study the thickness of the adhesive layer was set to a value of ca. 0.1 mm by means of fixture with a spring element. The joint length was 12.5 mm. For the joint width the overall width of the substrates was used. Figure 1 shows the lap shear joint of PEEK with the one-component adhesive.

Initial studies using untreated substrates reveal low lap shear strength combined with adhesive and cohesive failure patterns. Therefore, the substrates were pre-treated with an atmospheric plasma source. For this pre-treatment a rotational plasma source and a plasma-generator have been used. The substrates were moved through the plasma jet in a distance of 10 mm with a velocity of 6 mm/s. To measure the improvement of the surface energy a set of tests was employed which covers a measuring range from 35 to 56 mN/m in definite spacing.

The adhesives were applied on the substrates manually and the specimens were then mounted in a fixture during curing. The specimens bonded with the one-component adhesive were cured at a temperature of 180 °C and a duration of 70 min. The two-component adhesive was cured at a temperature of 130 °C for 30 min.

Table 1 – Geometry of lap shear test specimens

Material	Length [mm]	Width [mm]	Thickness [mm]
PEEK	100	20	3
PEI	83	10	4
PA66	100	20	3

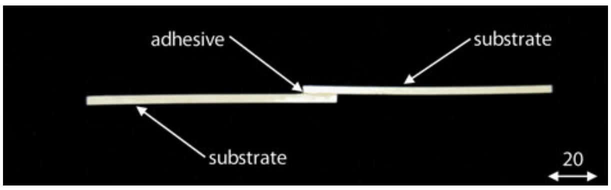


Figure 1 – Example of lap shear joint

The tensile test (according to DIN EN 527-1/2) and the shear tensile tests (according to DIN EN 1465) were performed on a material testing machine. This machine was equipped with a temperature test chamber. The testing temperature can be varied from −150 °C to 300 °C in this chamber. The samples were pre-conditioned for 15 min in the chamber at testing temperature. The specimens were exposed to testing temperatures equally spaced between 20 °C and 200 °C. The speed of loading was set to 10 mm/min for PEI and PA66 and 50 mm/min for PEEK respectively. After the shear tensile test the specimens were analysed according to DIN EN ISO 10365. In this experimental study the failure patterns were classified as substrate failure (SF) and adhesive or cohesive (AF/CF) failure. In this analysis the ratio of the substrate failure quantity to the sample quantity in percent was used as a characteristic number.

To identify characteristic temperatures, e.g. glass transition temperature, the materials were examined using thermal analysis. For this purpose the differential scanning calorimetry technique was used.

3 Experimental results

In order to analyse the materials a thermal analysis of the glass transition temperature of substrates and adhesives was performed. PEEK and PEI show a distinct glass transition temperature in the range of measurement, whereas PA66 reveals a broad transition between 50 °C and 100 °C. These findings correlate well with data from public material databases (CAMPUS).

In general, the glass transition temperatures of adhesives (based on an epoxy resin) show a significant dependence on their curing conditions. These conditions are governed by temperature and time within the curing process. For this study the thermal analysis on the adhesives was performed with the same thermal conditions in temperature and time as in the processing of the bonded lap shear specimens. A summary of the glass transition temperatures for all polymers is given in Table 2.

Except for the amorphous polyetherimide, all materials have a glass transition temperature which is within the testing range of 20 °C to 200 °C. The glass transition temperature of PA66 is significantly lower than that of the thermosetting adhesives. In contrast, PEEK exhibits

Table 2 – Glass transition temperatures

Material	Glass transition temperature T_G [°C]
Polyetheretherketone (PEEK)	150
Polyetherimide (PEI)	215
Polyamide 66 (PA66)	50-100
One-component adhesive (A1)	120
Two-component adhesive (A2)	50

Table 3 – Surface tension of substrates

Substrate	Surface tension [mN/m]	
	untreated	pre-treated
PEEK	38	≥ 56
PEI	44	52
PA66	38	48

a higher transitioning temperature than the adhesives. Therefore temperature can be confirmed to have a large influence on the mechanical behaviour of these materials.

The pre-treatment of the substrate with atmospheric plasma significantly increases the surface tension as shown in Table 3. Without a pre-treatment, the substrates, especially PEEK, could not be bonded properly due to poor wetting conditions of the adhesives on the untreated surfaces of the adherents [6].

The thermal analysis of the substrates and adhesives reveals distinct changes in the thermal behaviour in the range measured. Generally, thermoplastics show lower mechanical properties above the glass transition temperature compared to those below this state [6]. Therefore, one can assume that a bonded joint consisting of thermoplastic materials in combination with a thermosetting adhesive also shows this behaviour.

To study these material characteristics, lap shear tests (according to DIN EN 1465) were performed. The aim was to identify the influence of varying substrates, adhesives and even speeds of loading within the given temperature range on the lap shear strength (maximum load divided by bonding surface size) of bonded high-temperature resistant thermoplastics. Also their corresponding failure patterns were inspected to examine the properties at temperatures beyond the glass transition temperature of the polymers.

Figure 2 shows the influence of the testing temperature on the lap shear strength by comparing the adherents PEEK, PEI and PA66. These specimens were bonded with the one-component adhesive.

The lap shear strength of the bonded parts decreases with increasing test temperature within the observed temperature range. Specimens with adherents of PEEK and PEI reveal an absolute maximum of lap shear strength at a temperature of 80 °C. PA66 shows a steady decline of the lap shear strength. One can observe that above the glass transition temperature of the one-component adhesive (ca. 120 °C) all examined materials show an effective decrease in their mechanical properties. Below this characteristic temperature the mechanical properties depend on the temperature-dependent properties of the substrates. Parallel to the drop in mechanical properties the failure patterns alter from substrate failure (SF) to adhesive or cohesive failure (AF/CF) near the glass transition temperature of the adhesive.

Figure 2 shows that adherent materials of PEEK and PEI in combination with the one-component adhesive had higher lap shear strength at 80 °C compared to the strength at 20 °C. In general higher testing temperatures of adhesive joints (e.g. metal-based adherents and polymer-based adhesives) result in lower lap shear strength. However, the results of this study can be explained by the Volkersen-Model [6] where adherents and adhesives show mechanical properties in the same order of magnitude. This model describes the shear strength along the bonding surface by the following equation (terms are explained in Table 4):

$$\frac{\tau}{\tau_{max}} = \frac{2}{\omega}\tanh\left(\frac{\omega}{2}\right) \tag{1}$$

where

$$\omega^2 = 2\frac{G_a l^2}{E t t_a} \tag{2}$$

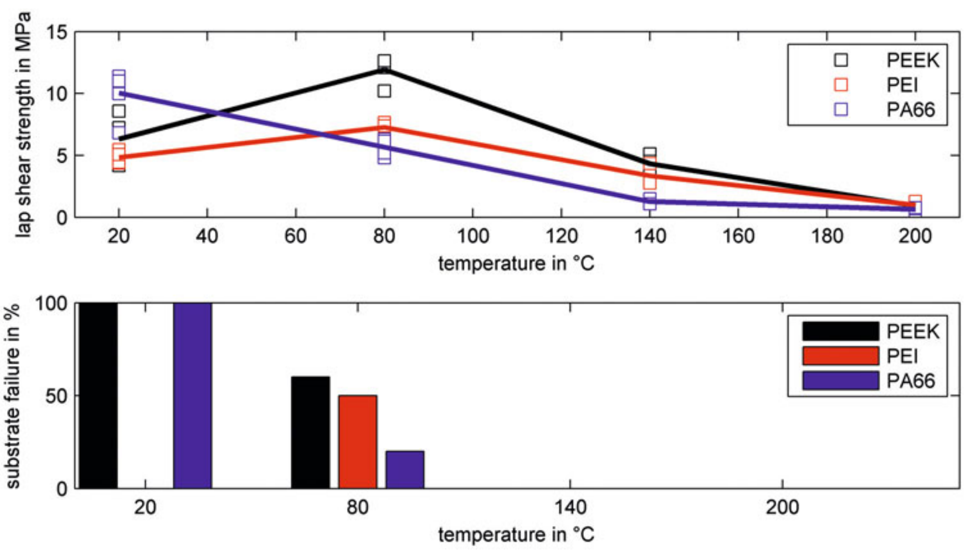


Figure 2 – Lap shear strength vs. temperature for PEEK, PEI and PA66 with one-component adhesive and a test speed of 10 mm/min

Table 4 – Parameters of the Volkersen-Model

Model parameter	Temperature			
	20 °C	80 °C	140 °C	200 °C
Configuration 1 : Adherent: PEEK, Adhesive: one-component adhesive				
Young's Modulus (adherent) E [MPa]	2 000	1 760	1 400	240
Shear Modulus (adhesive) G_a [MPa]	1 100	700	357	13
Configuration 2: Example values				
Young's Modulus (adherent) E [MPa]	2 000	1 500	1 000	500
Shear Modulus (adhesive) G_a [MPa]	1 000	1 000	600	300
Constant parameters				
Shear strength (adhesive) τ_{max} [MPa]	25	25	15	5
Adherent thickness t [mm]	3			
Adhesive thickness t_a [mm]	0.1			
Overlap length l [mm]	12.5			

The parameters of Configuration 1 in Table 4 are based on experimental data and the technical datasheet of the adhesive. The values for Configuration 2 do not show experimental data; they were selected to explain possible differences in mechanical behaviour. Figure 3 shows the calculated values for both configurations. One can observe that the temperature for the maximum lap shear strength is influenced by the combination of mechanical properties of the joint materials.

The same dependence on temperature can be found using a different adhesive with the same substrate conditions. In Figure 4 the lap shear strength of different adhesives and adherents (PEEK, PEI) is shown. The decline of lap shear strength is determined by the adhesive. The adhesives show a fundamental difference in their glass transition temperatures. The one-component adhesive shows an absolute maximum strength at 80 °C. In contrast the two-component adhesive shows a steady decrease. This temperature-dependent behaviour is directly linked to the adhesive's properties. Because its glass transition temperature is low (ca. 50 °C) the two-component adhesive exhibits a steady decrease of lap shear strength with increasing temperature. The one-component adhesive exhibits a change of failure pattern near its glass transition temperature. In the same way the failure patterns of the two-component adhesive turn over from substrate

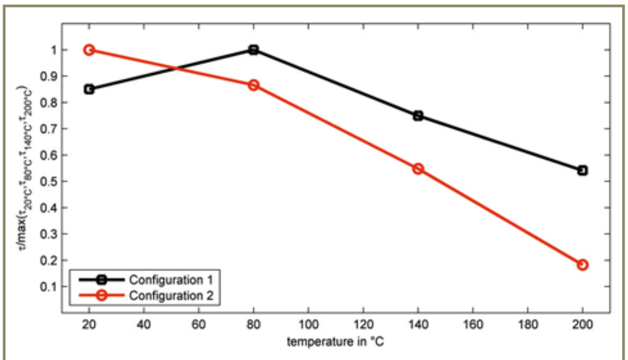


Figure 3 – Lap shear strength vs. temperature according to the Volkersen-Model

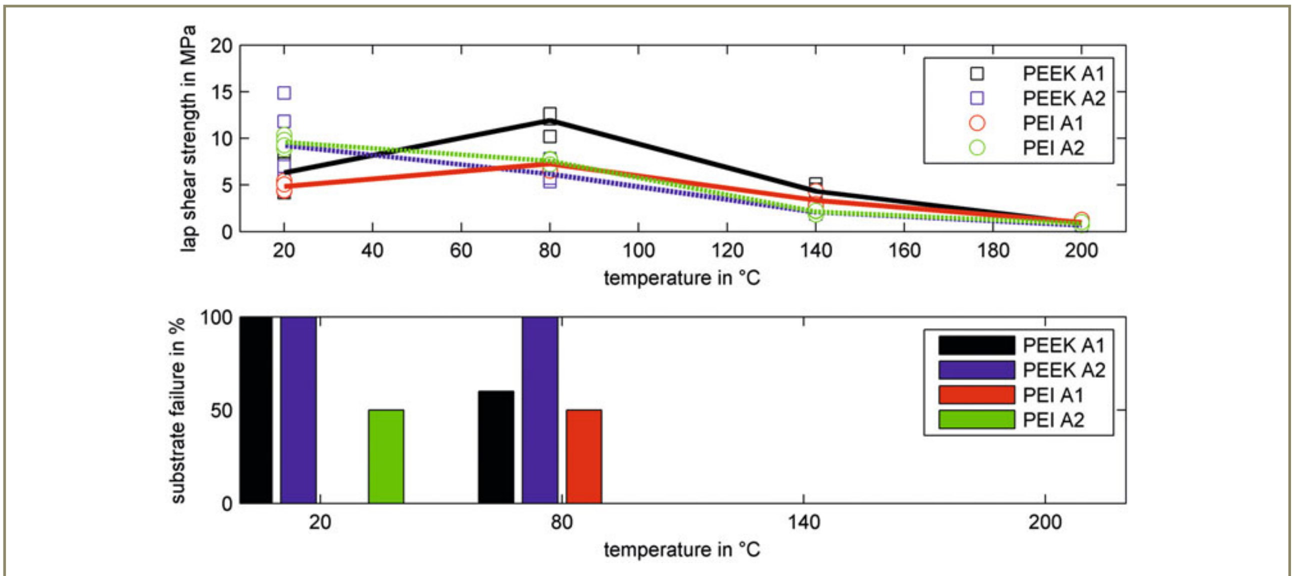


Figure 4 – Lap shear strength vs. temperature for PEEK and PEI with 1K and 2K adhesive

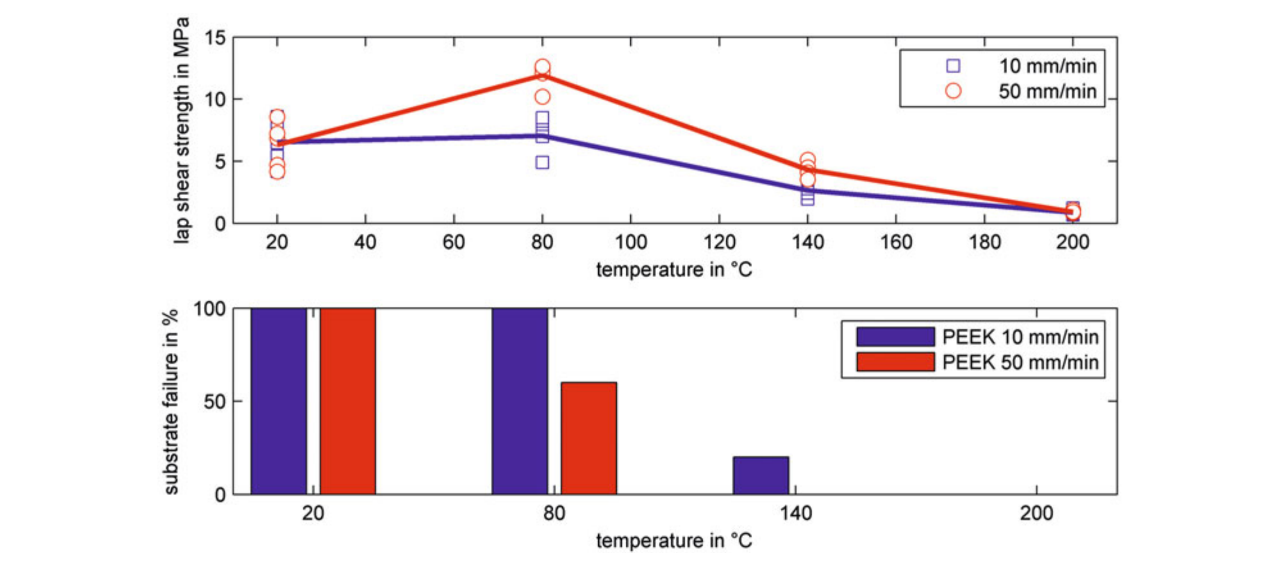


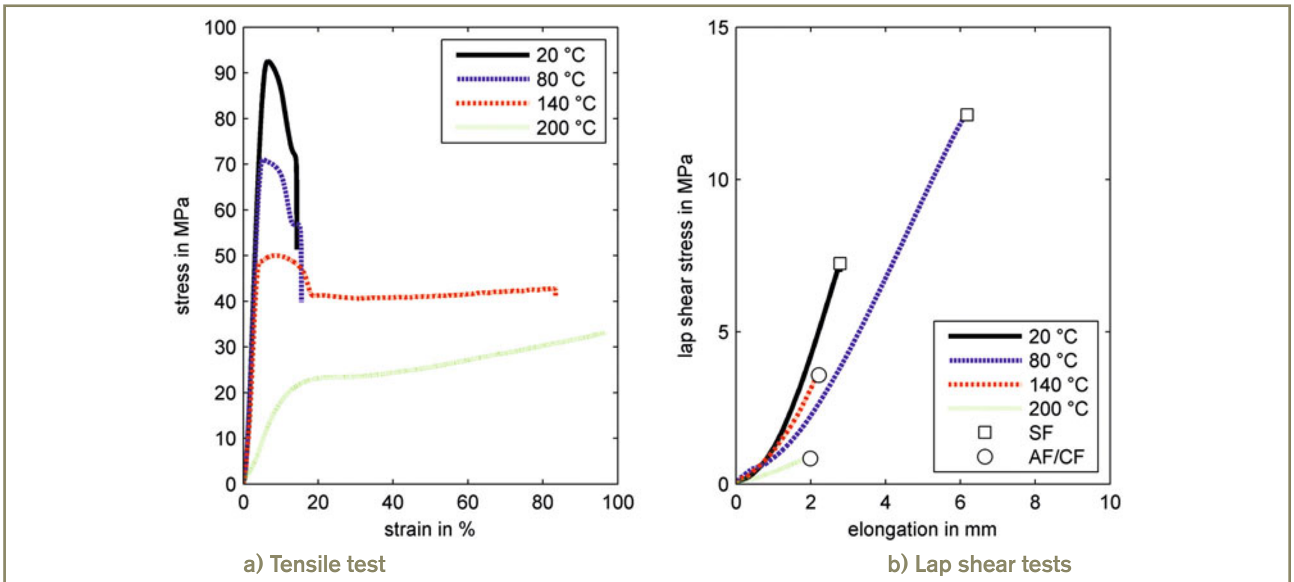
Figure 5 – Lap shear strength vs. temperature for PEEK bonded with one-component adhesive at varying speed of loading

(SF) to adhesive/cohesive failure (AF/CF) near the glass transition temperature of the adhesive.

Typically, thermoplastics exhibit a unique dependence on temperature and time which is commonly expressed by the time-temperature superposition principle [6]. To detect these material characteristics lap shear tests were also performed at two speeds of loading (10 mm/min, 50 mm/min). In Figure 5 the results for PEEK bonded with the one-component adhesive is shown.

Higher speeds of loading lead to a relevant change in the mechanical properties [7] also at higher temperatures in the range of glass transition temperature due to the visco-elastic material properties of polymers in general [6]. At temperatures greatly different (20 °C and 200 °C) from this characteristic temperature, the lap shear strength values are essentially the same. In the middle of the observed temperature range the lap shear strength increases when a higher speed of loading is chosen. Also the failure patterns change if the speed of loading is increased. At higher speeds the transition of the failure patterns are shifted to lower temperatures.

Since the thermoplastic substrates with thermosetting adhesives are very similar in their thermal dependence on mechanical properties a comparison between a tensile test of substrates and the shear tensile tests was performed. For this purpose PEEK was studied in tensile tests and bonded with the one-component adhesive in shear tensile tests. The results are shown in Figure 6. PEEK reveals a distinct yield stress below the glass transition temperature. Close to this characteristic temperature this material shows a high strain before failure. The failure patterns change near the glass transition temperatures which are obviously linked to the mechanical properties of the materials. One can assume that the different elongations based on the inhomogeneous Young's modulus of adherent and adhesive are responsible for the change in failure modes [6].



a) Tensile test
b) Lap shear tests

Figure 6 – Tensile test of adherents and lap shear tests (test speed of 10 mm/min)

4 Discussion

Based on the experimental results, a dimensionless model was introduced which describes the lap shear strength as a function of temperature near the point of glass transition. Therefore, only measurement data at 80 °C, 140 °C and 200 °C were taken into account.

Two dimensionless numbers were chosen. The first number [Equation (3)] represents the ratio Π_T of the temperature difference between a reference temperature T_∞ and current temperature T to the reference temperature. The second number Π_τ [Equation (4)] describes the relationship between the lap shear strength τ and the lap shear strength τ_∞ at a reference temperature. The reference temperature was set to 200 °C.

$$\Pi_T = \frac{T_\infty - T}{T_\infty} \tag{3}$$

$$\Pi_\tau = \frac{\tau - \tau_\infty}{\tau_\infty} \tag{4}$$

The correlation of the dimensionless numbers can be described by the following exponential function, Equation (5), with two unknown parameters.

$$\Pi_\tau = \exp(a\,\Pi_T)^b - 1 \tag{5}$$

By performing a least square fit of this function to the experimental data for different substrates and adhesives the unknown model parameters were determined. The mean values of these parameters are presented in Equations (6) and (7):

$$a = 1.33 \tag{6}$$

$$b = 2.80 \tag{7}$$

The coefficient of determination for these parameters is:

$$R^2 = 0.87 \tag{8}$$

The results lead to a function which represents the relationship between the dimensionless strength and the temperatures as given in Equation (9).

$$\frac{\tau - \tau_\infty}{\tau_\infty} = \exp\left(1.33\frac{T_\infty - T}{T_\infty}\right)^{2.80} - 1 \tag{9}$$

Due to this operation of modelling the governing dependencies can be generalized to a single curve as shown in Figure 7. The measured data have a high experimental standard deviation. Thus an error margin of ten percent of model parameters was taken into consideration. This range covers almost all measuring data as shown in Figure 7.

This empirical model shows the temperature dependence with respect to the lap shear strength of thermoplastic substrates and thermosetting adhesives at definite temperature levels. The model may be used to reduce time in examining adhesives for the bonding of high-temperature resistant thermoplastics due to the fact that the measurement of shear strength near the reference temperature is sufficient to describe the temperature dependence of mechanical properties. But, therefore, it is necessary to verify this model against other substrate materials and adhesives.

This first descriptive model of the relationship between lap shear strength and temperature should be also verified in future by a correlation with characteristic material properties.

5 Conclusion

The effect of the temperature dependence of thermoplastics bonded by thermosetting adhesives has been studied near the glass transition temperature of the adhesives. An empirical model was developed to describe the shear strength with respect to the temperature for different

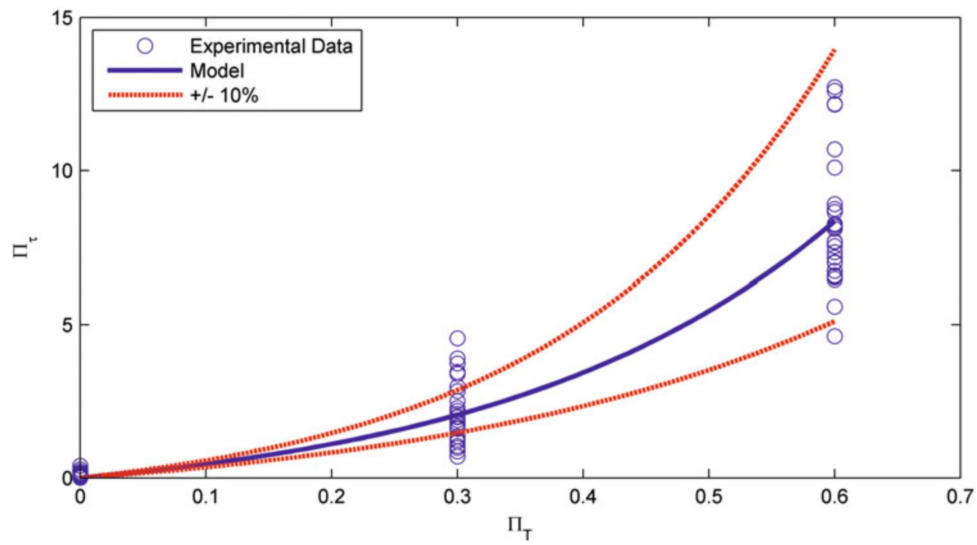


Figure 7 – Modelling of dimensionless lap shear strength vs. dimensionless temperature

substrates and adhesives. For this purpose dimensionless numbers are used. The results show that there are constant parameters which show an adequate accuracy with the experimental data. Based on this model, one can describe similar material combinations which are used at temperatures near or above the glass transition temperatures of a component. This may lead to a reduced time in the examination of this specific combination of adhesives and materials, because only a single point measurement of shear strength, at a definite temperature, could be sufficient to extrapolate this at higher temperatures.

Subsequent experimental investigations should include further combinations of substrates and adhesives to improve the prediction accuracy. In addition, the measurement setup should be improved as well, to reduce the high standard deviation of the experimental data. Furthermore, the model parameters should be correlated with properties one can measure at ambient temperatures. Also combinations of different substrates and adhesives should be investigated to adopt the model to a bond which is governed by three glass transition temperatures.

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