



Application of the Time–Temperature Superposition Principle to Predict Long-Term Behaviour of an Adhesive for Use in Shipbuilding

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Received: 17 April 2023 / Accepted: 10 August 2023 / Published online: 4 September 2023
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Abstract

The use of adhesives in the marine sector is rather limited at the time being, but their use in specific areas of the ship would be an advantage due, among other things, to their low weight and low stress concentration along the bonding joint. The aim of this work is to predict the long-term behaviour of the material, as this is a critical factor when using adhesive as a bonding method in ships, since its durability must be guaranteed throughout a previously defined life cycle. This can be predicted by applying the time–temperature superposition principle (TTS), which involves carrying out a test at different temperatures for each specimen, considerably reducing the test time. Two types of experiments have been carried out according with operation modes in dynamic mechanical analysis (DMA): a dynamic frequency sweep and a stationary creep test under constant stress, to check the behaviour of the adhesive under both dynamic and sustained loading. The master curve for the frequency study will be constructed in such a way as to cover the whole range of relevant vibrations that can occur on the vessel, while that for the creep test the curve obtained covers a range of 25 years, which is usually used as the minimum service life in shipbuilding. For both, a temperature range from room temperature to the maximum operating temperature of the material established by the manufacturer shall be studied.

Keywords Adhesive · Viscoelastic · Time temperature superposition (TTS) · Creep · Shipbuilding

1 Introduction

In current shipbuilding, the most widespread and consolidated bonding method is welding. Despite its wide use, this type of joint presents certain problems, such as high energy consumption or the increase in weight that it adds to the ship, which can be as large as 5% of the total weight. Following the current trend of searching for materials and techniques that are sustainable over time, this work presents a study of

an adhesive as a substitute for welding, which would solve the two major problems mentioned above.

Over the last few decades, countless studies have been carried out on adhesives and their possible uses in industry to replace traditional joining methods such as welding or riveting. The result of these studies has led to a widespread implementation of adhesives in industries such as aeronautical or automotive, but there are others more reserved to change such as the marine industry where their use is usually limited to small vessels or certain elements of offshore constructions. Even classification societies such as Bureau Veritas have developed guidelines regarding the use of adhesives on ships (Guidance Note NI 613 DT R00 E).

The use of adhesive bonds provides advantages such as low weight, corrosion resistance or joining multi-materials and lightweight materials [1]. Moreover, the characteristics of this type of joints will be key for the development of new technologies in the sector, such as low energy ship, Arctic ships and offshore or smart blade design for offshore wind power [2]. Delzendehrooy et al. [3] studied the current uses of this type of bonding in the marine sector as well as the

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methods for its correct application. Allan et al. [4] addressed the use of adhesives on modern warships, where aluminium is a widespread material, to repair cracks in this material or prevent crack growth, as aluminium often has fatigue problems and welding on board can be complicated due to the complexity of these ships.

Thermal and rheological properties are often used to evaluate the properties of adhesives and their suitability for specific applications [5]. One of the most important aspects to be taken into account will be the behaviour of the material throughout its life cycle, for which the time–temperature superposition principle will be used, which allows this type of study to be carried out by performing short tests at different temperatures [6]. In addition, the two most practised test types are the frequency study and the creep study, to assess the behaviour of the material for use at dynamically loaded and long-term loaded locations respectively. The function of the TTS is to shift the data obtained at different temperatures to construct a master curve at the chosen reference temperature. The most commonly used method for this process is that developed by Williams–Landel–Ferry (WLF) [7], although there are other formulations such as Arrhenius or Vogel–Fulcher–Tammann that can fit better adapted to the data depending on the case [8]. Alternatively, other studies use the time temperature–stress superposition principle (TTSSP) model proposed by Luo et al. [9, 10] for non-linear viscoelastic materials, whereby creep tests are performed at different temperature and stress values to construct the master curve.

There is extensive literature on TTS studies in polymers [11–13]. Dorléans et al. [14] demonstrated that for a given polymer, by applying this principle in both viscoelastic and viscoplastic tests, the shift factors obtained in the former can be implemented in the viscoplastic tests. One of the most analysed polymers is poly(methyl methacrylate) (PMMA) due to its good mechanical properties with high modulus and strength. Yao et al. [15] performed frequency tests at different temperatures to determine the ductile–brittle transition of the material. Wang et al. [16] use the TTSSP model to determine the creep behaviour of a PMMA. Guedes et al. [17] used the TTS in frequency and relaxation tests of a PMMA for application as an acrylic bone cement in bone implants.

There are also a number of studies of polymers for matrix application in composites such as fibre reinforced polymer (FRP) epoxy resins [18] and carbon filament reinforced PMMA [19]. Schalnath et al. [20] performed tests with both dynamic (frequency test) and static loading (creep test) to determine their degree of equivalence. From this it was concluded that for the first decade of the prediction the results have less than 10% disparity, while for longer predictions the difference is greater, and they are not similar. Miyano et al. [21] conducted a study on carbon fibre reinforced polymer (CFRP) laminates and performed a master curve of flexural

strength for static load, creep and fatigue tests. The result of the study is that, for this material, fulfilling the hypotheses proposed in the article, the fatigue strength curve can be obtained at an arbitrary combination of test parameters from the static load master curve or from the fatigue master curve for zero stress ratio.

For adhesives, the literature is less abundant because, as mentioned above, these materials are still under development. However, TTS studies can be found for adhesives with low modulus, high plasticity or for soft adhesive layers [22–24]. Regarding adhesive bonds, Carneiro Neto et al. [25] studied the evolution of the lifetime and fracture energy of the bond under creep loads at different percentages of the maximum load capacity of the joint, showing a significant decrease in the creep life beyond 70% of the maximum load. Due to the nature of adhesive bonding applications, it is common practice to apply TTS for creep tests, some studies in this area are for metal–composite [26], composite–composite [27] or aluminium–crystal bonding [28]. Wang et al. [29] performed a dynamic mechanical analysis using TTS to characterise an epoxy adhesive, and then applied it as a reinforcement material for a beam under creep loading by means of a finite element simulation, obtaining a considerable reduction in the properties of the reinforced beam at temperatures close to the glass transition temperature.

There are other factors that can affect the properties of adhesives, such as humidity. Feng et al. [30] studied the behaviour of an epoxy adhesive under different humidity and temperature conditions, obtaining an equivalence between different combinations of both parameters. There are also alternatives to the traditional TTS, in which factors such as ageing or the concentration of a certain component in the material are considered. Among them, Barbero [31] studied the time–temperature–age superposition model in which he addresses the effect of temperature, for relatively short periods of time, and that of age, in order to obtain the combined effect of both factors. Time–temperature–water ageing has been applied to epoxies allowing predictions of several decades under creep loads and considering the influence of these conditions [32]. Another variant of this theory is discussed by Krauklis et al. [33] in which different degrees of plasticisation of the material are considered in the implementing the superposition principle.

All types of loads can occur on a ship, with a distinction being made between dynamic and static loads, the former are usually produced by the action of the propeller, machinery or waves, whereas for static loads the cause will depend on the particular case. The effects of dynamic loads on the ship can take the form of global vibrations of the ship–beam assembly, as well as local vibrations, some of the most common being that of the superstructure or the double bottom in places such as the engine room due to the action of the main engine. In terms of frequency, the greatest adverse effects on the

structure occur up to about 20 Hz, although vibrations of considerably higher frequencies may occur, which will have a lesser structural impact and a greater effect in relation to noise [34]. In relation to static loads for locations where adhesives would be used, these can occur for example in bulkhead or reinforcement joints, or even bonded studs, and these joints can be subjected to many types of loading, from tensile or flexural, to peeling.

With regard to the ambient conditions that may be encountered on a ship, these vary according to the space in question. For the accommodation areas, according to ISO 7547, temperatures of about 20 °C to 30 °C are considered in interior spaces depending on the space and the season, with humidities of up to 50% in the case of summer. In relation to other areas of the ship where conditions will be more critical, such as the engine room, an ambient temperature of 45 °C at 60% relative humidity is taken as a reference in accordance with UR M28 for machinery installations of the International Association of Classification Societies (IACS) and a temperature of up to 55 °C should also be considered for this type of environment. In addition, hot spots may occur on the ship such as sun-exposed areas, where, for instance, temperatures of up to 70 °C have been recorded in deck joints [35]. Although it is not the subject of this paper, negative temperatures or even 100% relative humidity may also occur in certain areas of the hull under certain conditions, but these are not very typical in places where adhesives are commonly used.

In this paper, the time–temperature superposition principle is applied to predict the behaviour of a methyl methacrylate (MMA) structural adhesive for use in the shipbuilding industry. This is highly relevant because it allows to know and predict the durability of an MMA with the aim of incorporating it as a bonding material for naval steel and therefore providing an alternative joining method to welding. There are currently no studies that address this aspect of adhesives with a focus on the marine sector. For this purpose, two test methods were used, one with dynamic loads and the other with static loads, using a DMA. In the first one, a frequency test is carried out to check the response of the material to this type of loads, covering with the master curve both the low frequency vibrations, from 0 to 100 Hz, and higher order frequencies and harmonics, with values above 100 Hz. The second type of test will be a creep test for sustained loads that may occur on the ship. In addition, the temperature range studied, from 30 to 90 °C, covers the upper part of the range of use of the adhesive.

2 Theoretical Background

2.1 Viscoelastic Behaviour

A solid in its elastic zone has a defined shape, when a force is applied to the material it deforms and stores energy and when the force ceases it returns to its original shape releasing that energy, whereas a viscous liquid has no defined shape and when it receives a force it flows irreversibly. The properties of polymers can be found throughout the range between the two types of materials above. This material behaviour combining the properties of solids and liquids is called viscoelasticity. Thus the modulus of the polymers depends on time and temperature and can vary greatly depending on these [36].

On the basis of Hooke’s law for an ideal elastic solid (Eq. 1), the modulus of a material (E) is the factor of proportionality between the applied stress (σ) and the deformation obtained (ε) or vice versa:

$$E = \frac{\sigma}{\varepsilon} \tag{1}$$

Using a dynamic mechanical analyzer (DMA) and subjecting the specimen to controlled alternating deformation, the applied stress is measured [37], and the strain (Eq. 2) and stress (Eq. 3) can be defined as follows:

$$\varepsilon = \varepsilon_0 \sin(\omega t) \tag{2}$$

$$\begin{aligned} \sigma &= \sigma_0 \sin(\omega t + \delta) \\ &= \sigma_0 \sin(\omega t) \cos(\delta) + \sigma_0 \cos(\omega t) \sin(\delta) \end{aligned} \tag{3}$$

where ε_0 and σ_0 are the strain amplitude and the stress amplitude respectively, ω is the frequency, t being the time, and δ represents the phase angle. In the stress equation, the first summand is in phase with the strain and the second is 90° out of phase with the strain. Thus the equation can be rewritten as a function of the components of the modulus (Eq. 4).

$$\sigma = \varepsilon_0 E' \sin(\omega t) + \varepsilon_0 E'' \cos(\omega t) \tag{4}$$

where E' is the term in phase with the strain (Eq. 5), called the storage modulus, and is related to the ability of the material to store energy under elastic deformation, whereas E'' is the out of phase term (Eq. 6), called the loss modulus, and represents the ability of the material to dissipate stress through heat.

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \tag{5}$$

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta \tag{6}$$

The complex sum of these two terms is the so-called complex modulus (E^*) (Eq. 7). On the other hand, the ratio

between E'' and E' is known as $\tan \delta$ or loss angle (Eq. 8).

$$E^* = \frac{\sigma_0}{\varepsilon_0} \exp(i\delta) = \frac{\sigma_0}{\varepsilon_0} (\cos(\delta) + i \sin(\delta)) = E' + iE'' \quad (7)$$

$$\tan \delta = \frac{E''}{E'} \quad (8)$$

2.2 Time–Temperature Superposition Principle

Using the time–temperature superposition principle, the master curves for the viscoelastic parameters of the adhesive will be constructed by shifting the data obtained at each temperature on the vertical and horizontal axes as required to obtain a good matching of the overlapping data. For this purpose, the shift factors a_T (horizontal axis, Eq. 9) and b_T (vertical axis, Eq. 10) are used [6, 7].

$$a_T = \frac{f}{f_0} \quad (9)$$

$$b_T = \frac{E(T_0)}{E(T)} \quad (10)$$

where f and f_0 are the test frequency and the shifted frequency respectively, meanwhile $E(T_0)$ and $E(T)$ represent the value of a viscoelastic parameter obtained in the test and its shifted value respectively. This way, the curves will be plotted as a function of the reduced frequencies ($a_T f$). The shift factors used will be compared with the theoretical values obtained with the Williams–Landel–Ferry model (Eq. 11) and the Arrhenius model (Eq. 12) since, depending on the material, it may adapt better to one model or the other [8]. Although, in general, the Arrhenius equation works best when the test temperatures are higher than $T_g + 100$ °C, this will not be our case and will only be calculated as a check.

$$\log a_T = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)} \quad (11)$$

where C_1 and C_2 are calculated constants and T and T_0 are the current temperature and reference temperature respectively, in K or °C degrees.

$$\log a_T = -\frac{E_A}{2.303R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (12)$$

where E_A is the calculated activation energy, in J/mol, R is the gas constant, equal to 8.314 J/mol K, and T and T_0 are the current temperature and reference temperature respectively, both in K.

2.3 Creep

Creep is defined as the tendency of a viscoelastic material to deform under the action of a constant stress; moreover, for a given load the deformation increases with temperature. The parameters analysed in this test will be the flexural modulus (E), the strain and the creep compliance (J). Creep compliance is defined as the ratio of the strain to the applied load, in other terms it will be the inverse of the modulus (Eq. 12), in this case in flexure [36].

$$E(t) = \frac{\sigma}{\varepsilon(t)} = \frac{1}{J(t)} \quad (13)$$

In this case, for the master curves, instead of using the reduced frequency scale, the curves are presented as a function of the reduced time, t_0 (Eq. 14), calculated in an analogous way to the frequencies.

$$a_T = \frac{t}{t_0} \quad (14)$$

3 Experimental

3.1 Adhesive

The adhesive selected to conduct this research is a two-part methyl methacrylate (Plexus MA530), recommended for use in thermoplastics, metals, and composites. It is applied in a 1:1 ratio, no priming required. Its working time is 30 to 40 min, and its curing time is 90 min. The operating temperature of this adhesive is between -40 and 82 °C. The adhesives, technical data and safety data sheets were supplied by the manufacturer.

3.2 Specimen Manufacturing

The adhesive specimens were manufactured by injecting the adhesive into a mould according to the French standard NF T 76-142, using a 1 mm thick polytetrafluoroethylene (PTFE) sheet instead of the silicone frame mentioned by da Silva et al. [38], as shown in Fig. 1. The mould is placed in a hydraulic press and a pressure of 20 MPa was applied to ensure uniform thickness of the specimens throughout the adhesive sheet and to avoid bubble formation.

From the adhesive sheet, $60 \times 10 \times 1$ mm specimens are cut to fit the dimensions of the geometry used in the DMA and seeking to make the edges as straight and parallel as possible. In this way, 7 specimens of 60 mm length, (9.97 ± 0.20) mm width and (1.06 ± 0.06) mm thickness were obtained. A sample of 10 mg is taken from the same sheet for thermogravimetric analysis. The specimens were left to



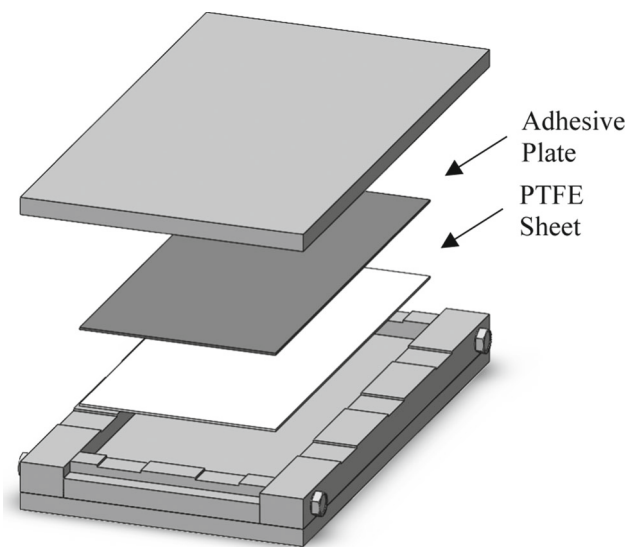


Fig. 1 Exploded view of the mould and the adhesive sheet

cure for 1 month at room temperature to ensure proper curing of the material.

3.3 Experimental Techniques

3.3.1 Thermogravimetric Analyzer (TGA)

Thermogravimetric analysis was carried out using the TA Instruments SDT 2960 model. A 10 mg sample of the adhesive was taken and ramped from room temperature to 700 °C at a rate of 15 °C/min under an air atmosphere.

3.3.2 Dynamic Mechanical Analyzer (DMA)

Multiple tests were performed using a TA Instruments DMA 2980 with the Dual Cantilever clamp. Starting from the 7 prepared specimens, the first one was used for a Temperature Sweep test to determine the glass transition temperature (T_g) of the adhesive, performing the test at 1 Hz and between 60 and 120 °C.

For the remaining 6 specimens, 3 consecutive tests were performed: first a Strain Sweep at 1 Hz frequency and from 1 to 1500 μm to obtain the amplitude to be used for the following tests and to ensure that this works well for all specimens, second a Frequency Sweep from 0.01 to 100 Hz was performed with the amplitude determined previously and taking 4 data per decade, both at room temperature, finally, either a Frequency Sweep-Temperature Step test or a Creep-Temperature Step test was performed dedicating 3 specimens to each of these.

For the Frequency Sweep-Temperature Step test, the same parameters used in the Frequency Sweep were taken for temperatures from 30 to 90 °C with increments of 10 °C and

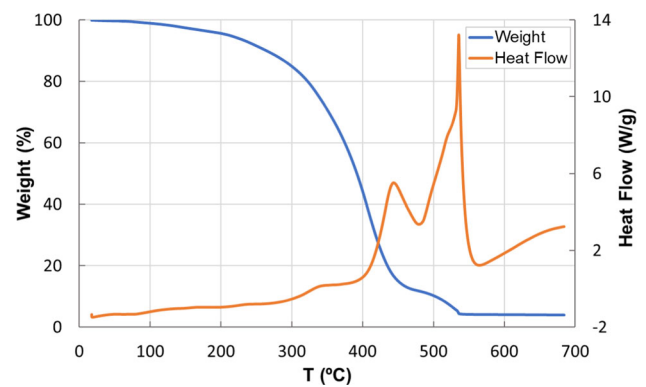


Fig. 2 TGA results for methyl-methacrylate structural adhesive

5 min of soak time, covering from room temperature to the maximum operating temperature of the material.

For the Creep-Temperature Step test, the same temperatures are covered as in the previous case and with a load of 5 MPa. The conditions for each cycle of the test, 5 min of soak time, 10 min of loading and 10 min of recovery are established.

4 Results

4.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was carried out to determine the behaviour of the adhesive with temperature and confirm that the specimens will not lose a substantial amount of mass during TTS. From this in Fig. 2 it can be concluded that, for the operating temperature of the adhesive, the loss in weight of the material is not significant and will not be a problem for the tests.

Furthermore, from the Heat Flow curve it is possible to know whether the adhesive is fully cured or not since curing is an exothermic reaction and would be reflected in an exothermic peak in the first part of the curve (from 0 to 300 °C), so it can be concluded that the adhesive is properly cured.

4.2 Dynamic Mechanical Analysis (DMA)

4.2.1 Strain and Frequency Sweeps

The manufactured adhesive specimens were first subjected to a strain sweep, which consists of exposing the sample to a controlled sinusoidal deformation with an increasing amplitude, from 1 to 1500 μm , at a frequency of 1 Hz, thereby selecting the test amplitude that makes the material work in its elastic zone for subsequent tests. After this, a frequency sweep was performed, in this case the sinusoidal deformation keeps constant the amplitude, which was selected from the

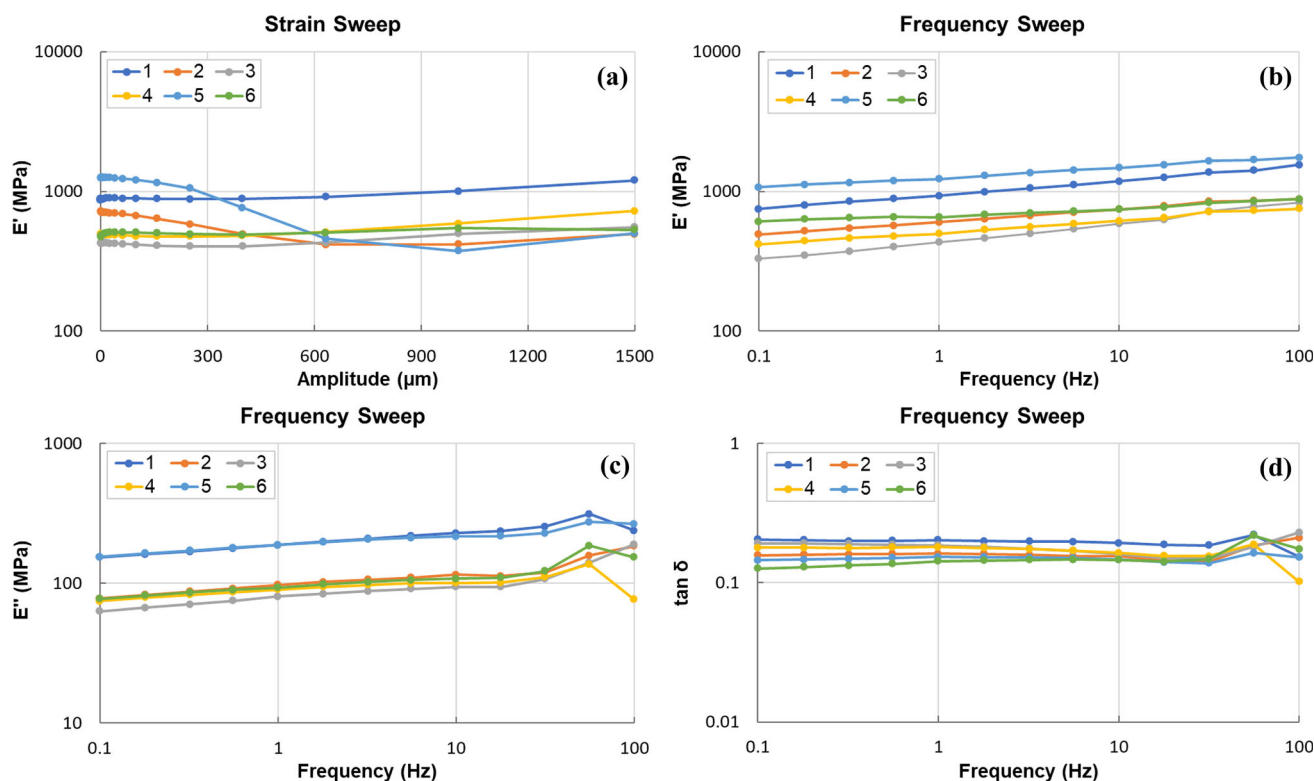


Fig. 3 Strain and frequency sweep results for methyl-methacrylate structural adhesive. Strain sweep: **a** storage modulus (E'). frequency sweep: **(b)** storage modulus (E'), **(c)** loss modulus (E'') and **(d)** $\tan \delta$

previous test, and the frequency is changing between 0.1 and 100 Hz, taking 4 points per each decade of the logarithmic scale.

The aim of this procedure is to check the reproducibility of the tests carried out with the different specimens and to increase the number of the data in order to enhance the reliability of the master curve of the material in the subsequent sections.

From the Strain Sweep test (Fig. 3a) it was determined that the adhesive has a fairly constant response up to 100 μm . The amplitude selected for the Frequency Sweep will be 50 μm , leaving a small safety margin with respect to the observed value. On the other hand, in the Frequency Sweep it is observed that, for all specimens, there is a singular point in the graphs at 56 Hz, which can be seen in the loss modulus and $\tan \delta$ graphs. This is probably related to a resonance phenomenon associated to the sample geometry and internal features of the instrument. Meanwhile for 100 Hz, the highest of the test frequencies, the greatest dispersion in the results is found.

4.2.2 Glass Transition Temperature (T_g)

A Temperature Sweep test was performed to determine the glass transition temperature (T_g) of the material. This test

was performed with the DMA instead of doing a differential scanning calorimetry (DSC) because the former has a higher sensitivity to show this parameter. The experiment involves subjecting the adhesive to the 50 μm deformation, obtained in the previous tests, at a frequency of 1 Hz and increasing the temperature from 60 to 120 $^{\circ}\text{C}$.

What is sought in this test is a maximum $\tan \delta$, meaning that the ratio between the viscous behaviour, represented by the loss modulus (E''), and the elastic behaviour of the material, represented by the storage modulus (E'), is at its maximum. Figure 4 shows that the glass transition temperature is about 87.5 $^{\circ}\text{C}$, which leaves this material within the T_g range of commercial MMAs, from 85 to 165 $^{\circ}\text{C}$ [39].

4.2.3 Master Curves

In this section, the construction of the master curve will be carried out, taking the average value of the data obtained for the three specimens dedicated to each type of test. This way, a single master curve more representative of the material will be presented for each of the selected parameters. The displacement of the curves was carried out using the TRIOS software of TA Instruments.

The reference temperature selected is 40 $^{\circ}\text{C}$, since this is a temperature that is likely to be encountered in the ship's

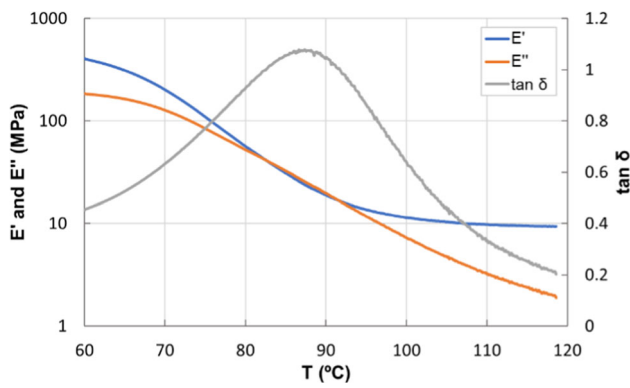


Fig. 4 Temperature sweep results for methyl-methacrylate structural adhesive

engine room on a regular basis and will also be one of the most adverse ambient temperatures that will occur on the vessel. It would also be possible to select 50 °C as a reference for the displacement, as this would cover more critical temperature conditions that may occur at certain times at this location, but 40 °C is chosen since the master curves obtained for the frequency test reach 10,000 Hz and higher frequencies would be unnecessary since their effect on the ship is negligible, while for the creep test the obtained master curve covers a range of about 25 years, which is the design life for the ship's structure as established in Recommendation No.106 "IACS Guideline for Rule Development—Ship Structure".

The master curves of the following viscoelastic parameters are constructed: storage modulus (E'), loss modulus (E''), $\tan \delta$ and complex modulus (E^*), for the Frequency Sweep-Temperature Step test; flexural modulus (E), creep compliance (J) and strain (ϵ), for the Creep-Temperature Step test. In the case of the former, it is plotted as a function of the logarithm of the reduced frequencies ($a_T \cdot f$) and in the case of the latter, it is plotted as a function of the reduced time ($a_T \cdot t$). The data obtained prior to the displacement of the curves is also shown in the graphs below (Figs. 5, 6).

4.2.4 Curve Shifting

From the TRIOS data the shift factors were obtained on both the horizontal (a_T) and vertical (b_T) axes. In addition, the coefficients C_1 and C_2 of the Williams–Landel–Ferry equation and the activation energy (E_A) of the Arrhenius equation are determined. In this way it can be checked how the horizontal shift factors fit both methods.

For the WLF model the constants obtained are $C_1 = 58.96$ and $C_2 = 269.87$, meanwhile for the Arrhenius equation the resulting activation energy is 378.15 kJ/mol, in the Frequency Sweep-Temperature Step test. For the Creep-Temperature Step test the WLF constants are $C_1 = 52.60$ and $C_2 =$

313.48 and the Arrhenius activation energy has a value of 296.57 kJ/mol.

The horizontal shift factors a_T fit the WLF model with a coefficient of determination (R^2) of 0.9955 and the Arrhenius model with an R^2 of 0.9954, all of this for the Frequency Sweep-Temperature Step test (Fig. 7a). On the other hand, it can be seen from Fig. 7b that the logarithms of the vertical and horizontal shift factors have a linear relation.

For the creep test (Fig. 8) a_T has a coefficient of determination of 0.9971 with the WLF model and 0.9951 with de Arrhenius model. Some of the viscoelastic parameters obtained with this test, such as the Creep Compliance, use the inverse of the vertical shift factor to construct their master curve.

4.2.5 Validation Criteria

The following validation criteria have been checked: the shift factors (a_T) conform to those of WLF or Arrhenius, the same shift factors work for all viscoelastic parameters, the Van Gorp–Palmen plot must be a smooth and continuous curve and the Cole–Cole plot must be a smooth and continuous curve [40]. The Van Gorp–Palmen graph plots phase angle (δ) versus complex modulus (E^*) and the Cole–Cole graph plots loss modulus (E'') versus storage modulus (E'), all of these are viscoelastic parameters obtained only in the Frequency Sweep-Temperature Step test, therefore these conditions do not apply to the Creep test.

The shift factors for both types of tests have already been presented in the previous section (Figs. 7, 8) and the Master Curves for the different parameters obtained can be seen in this same section. In them it can be seen that the shift factors used work for all the graphs and therefore this criteria is fulfilled.

The Van Gorp–Palmen and Cole–Cole plots present the parameters obtained in the test, all temperature-dependent, in a time-independent manner [41]. The second of these also shows the relationship between the real (E') and imaginary (E'') components of the adhesive modulus [42]. Smoothness and continuity in the curve in each of them is indicative of a good construction of the Master Curve.

Despite the presence of some singular points, produced at the higher frequencies (100 Hz, 56 Hz, 31.6 Hz and 17.8 Hz) in some of the temperatures, both curves are considered to be sufficiently smooth and show good continuity. With this, all the validation criteria mentioned above have been checked and therefore the geometrical construction of the master curves for both types of tests is deemed to be correct (Fig. 9).

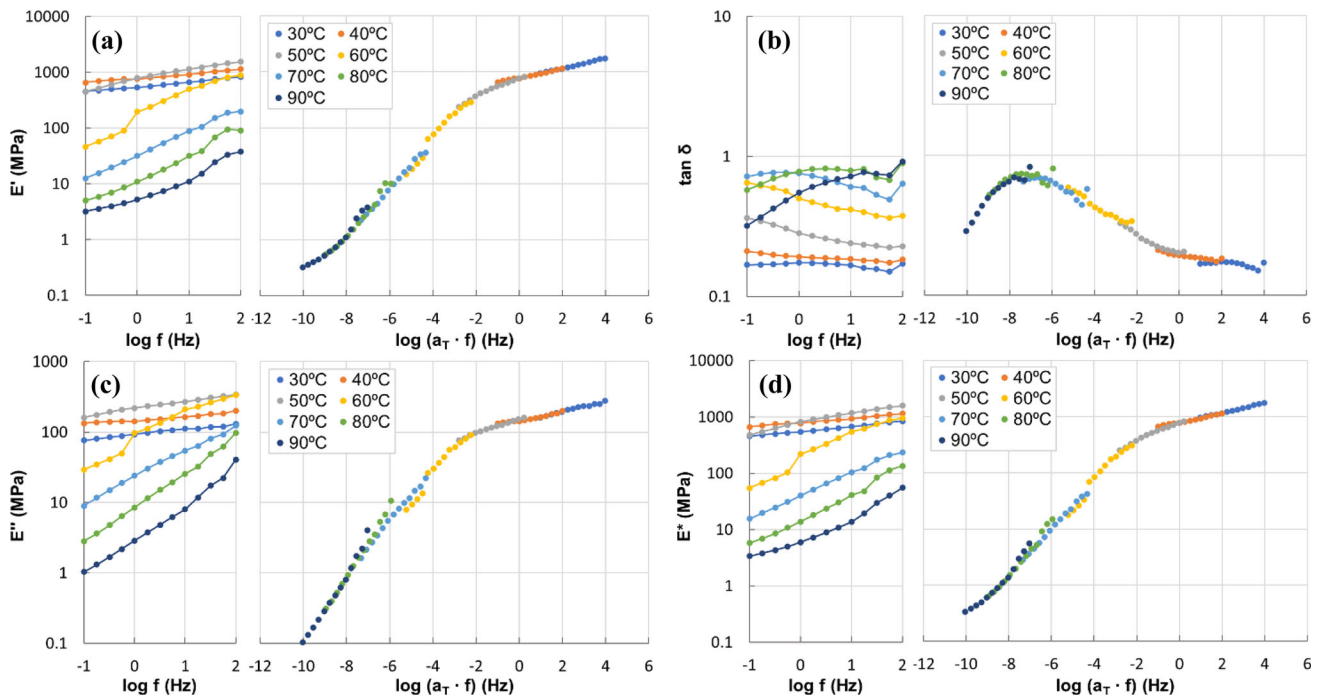


Fig. 5 Obtained data and master curves for methyl-methacrylate structural adhesive in a Frequency Sweep-Temperature Step test. **a** Storage modulus (E'), **b** $\tan \delta$, **c** loss modulus (E'') and **(d)** complex modulus (E^*)

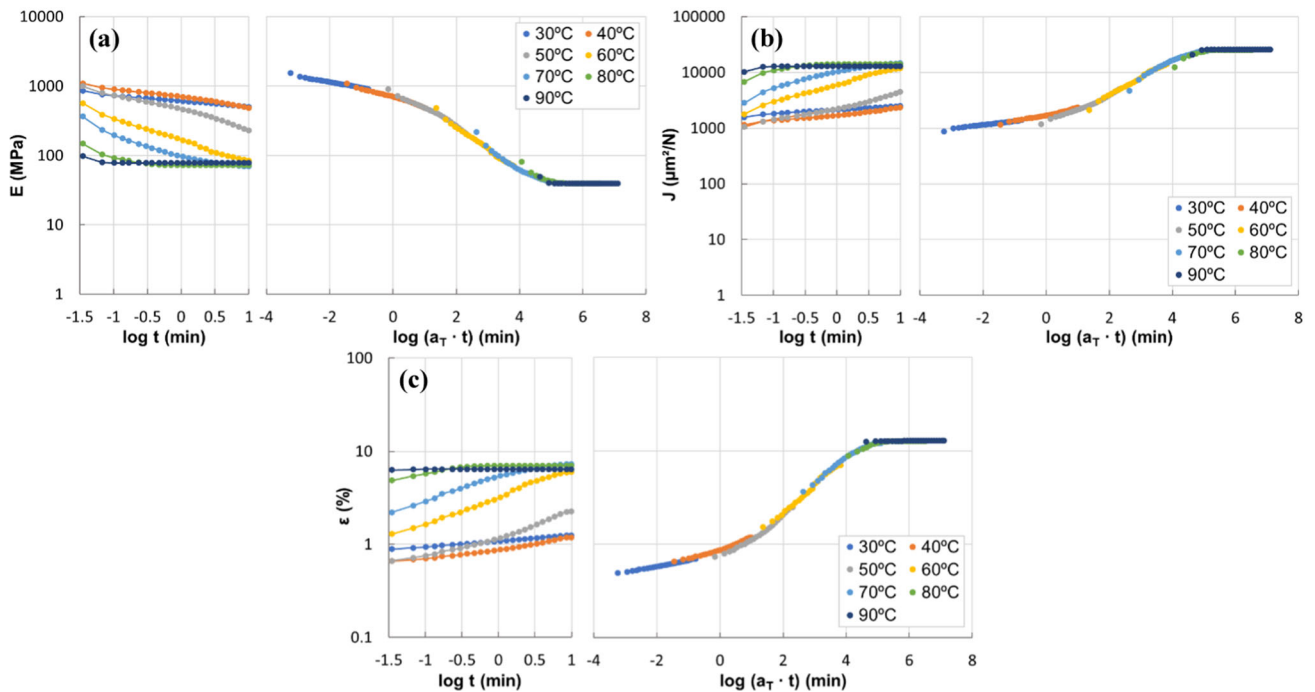


Fig. 6 Obtained data and master curves for methyl-methacrylate structural adhesive in a Creep-Temperature Step test. **a** Flexural modulus (E), **b** creep compliance (J) and **c** strain (ϵ)

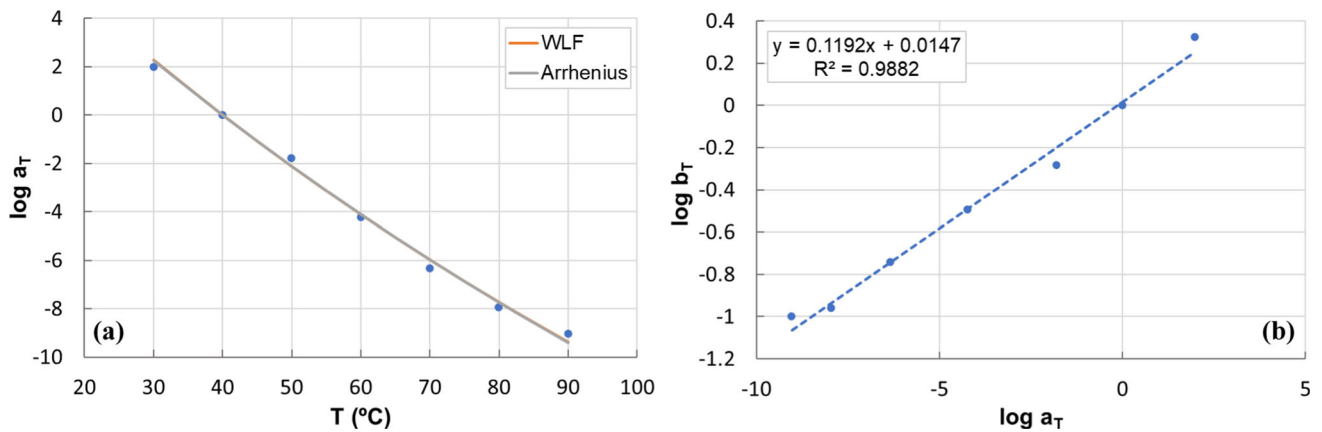


Fig. 7 Shift factors for Frequency Sweep-Temperature Step test. **a** Fitting of a_T to the WLF and Arrhenius models. **b** Relation between the vertical and horizontal factors

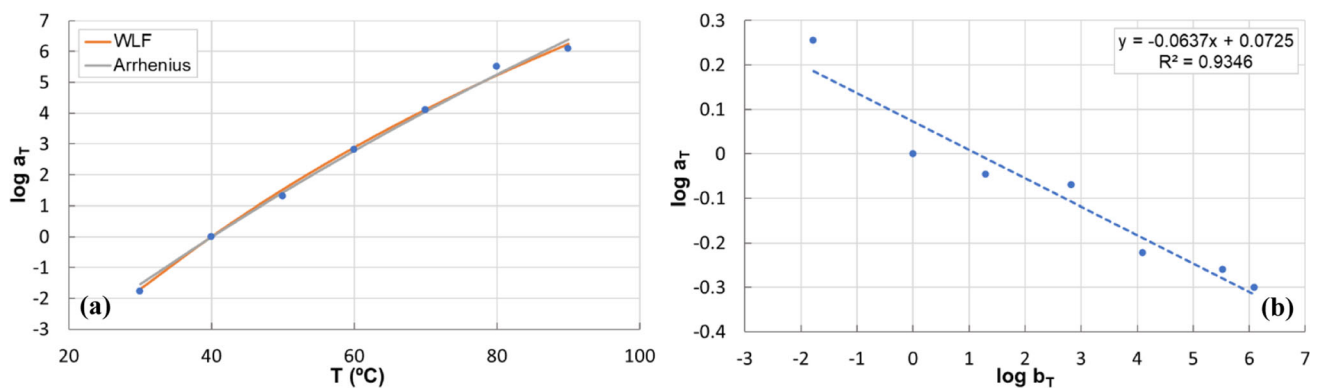


Fig. 8 Shift factors for Creep-Temperature Step test. **a** Fitting of a_T to the WLF and Arrhenius models. **b** Relation between the vertical and horizontal factors

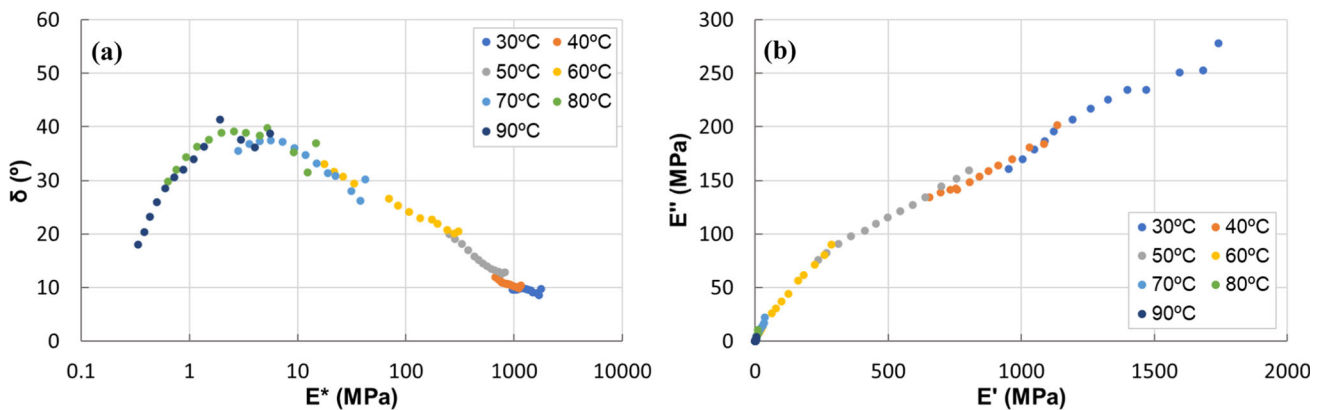


Fig. 9 Validation plots for Frequency Sweep-Temperature Step test. **a** Van Gurp-Palmen plot. **b** Cole–Cole plot

5 Conclusions

This paper studies the long-term behaviour of a structural adhesive for use in the shipbuilding industry under two types of loading, firstly the dynamic loads that could occur on a ship due to vibrations and secondly the sustained static loads

that can occur on virtually every structural element where the adhesive is used, such as a bulkhead-hull joint.

The reduced frequencies used in the Frequency Sweep-Temperature Step test range from 0 to 10,000 Hz, covering both low frequencies, which can produce resonance effects in the ship’s structure, and high frequencies, with less structural effect. Time obtained in the Creep-Temperature Step

test is approximately 25 years, which is the design life for the ship structure as established by IACS. In addition, the master curves obtained by TTSP have been validated for both types of tests, complying with the criteria established in Sect. 4.2.4, the horizontal shift factors fit the WLF and Arrhenius models, the shift factors work for all the viscoelastic parameters of each test and the Van Gurp–Palmen and Cole–Cole plots are smooth and continuous for the frequency test.

Concerning the results obtained from the Frequency Sweep–Temperature Step test, it can be concluded that the modulus decreases in the order of 70–80% from 10,000 Hz to the inflection point shown in the master curve at 0.01 Hz, after which the load can be considered quasi-static and the reduction of the parameters is much smaller. Furthermore, in the 1–20 Hz range, which is where the greatest effects of dynamic loading tend to occur, and where resonance effects are more likely to occur, the modulus reduction is less substantial.

While in relation to the results of the Creep–Temperature Step test, exemplifying the data obtained for the flexural modulus, it is observed that under a load of 5 MPa there is a reduction of 97% of the initial value when the curve reaches 3 months and reaching an apparent limit of 40 MPa.

Acknowledgements The authors gratefully acknowledge IACOBUS Program from the European Strategic Group of Territorial Cooperation Galicia/North of Portugal for a research fellowship. The authors also wish to acknowledge and thank the support provided by Krafft S.L.U. Spain (ITW Performance Polymers).

Funding Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature. The authors of this research have not received funding for this work. They have received the adhesive and are grateful to the commercial company. Funding for open access charge: Universidade da Coruña/CISUG.

Declarations

Conflict of interest One of the authors, Ana Álvarez García, has made a stay with the IACOBUS program that has allowed her to learn certain techniques of manipulation of the adhesive that she has applied. For finally, the authors did not receive support from any organization for the submitted work. All authors certify that they have no affiliations with or involvement in any organisation or entity with any financial or non-financial interest in the subject matter or materials discussed in this manuscript.

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