# Package ‘TTS’

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**Type** Package

**Title** Master Curve Estimates Corresponding to Time-Temperature Superposition

**Version** 1.0

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**Depends** R (>= 3.0.1), mgcv, sfsmisc, splines

**Description** Time-Temperature Superposition analysis is often applied to frequency modulated data obtained by Dynamic
Mechanic Analysis (DMA) and Rheometry in the analytical chemistry and physics areas. These techniques provide estimates of material mechanical properties (such as moduli) at different temperatures in a wider range of time. This package provides the Time-Temperature superposition Master Curve at a referred temperature by the three methods: the two wider used methods, Arrhenius based methods and WLF, and the newer methodology based on derivatives procedure. The Master Curve is smoothed by B-splines basis. The package output is composed of plots of experimental data, horizontal and vertical shifts, TTS data, and TTS data fitted using B-splines with bootstrap confidence intervals.

**License** GPL (>= 2)

**LazyData** yes

**NeedsCompilation** no

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## R topics documented:

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TTS-package *Estimates of material properties by Time-Temperature Superposition (TTS) analysis*

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## Description

TTS analysis is often applied to frequency modulated data obtained by Dynamic Mechanic Analysis (DMA) and Rheometry in the analytical chemistry and physics areas. These techniques provide estimates of material mechanical properties (such as moduli) at different temperatures in a wider range of time. This package provides the Time-Temperature superposition Master Curve at a referred temperature by the three methods: the two wider used methods, Arrhenius based methods and WLF, and the newer methodology based on derivatives procedure. The Master Curve is smoothed by B-splines basis. The package output is composed of plots of experimental data, horizontal and vertical shifts, TTS data, and TTS data fitted using B-splines with bootstrap confidence intervals.

## Details

| | |
|---|---|
| Package: | TTS |
| Type: | Package |
| Version: | 1.0 |
| Date: | 2015-09-14 |
| License: | GPL >= 2 |

The main functions and data frame are `TTS`, `PLOT.TTS` and `PC`

## Author(s)

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## References

Naya, S., Meneses A., Tarrio-Saavedra, J., Artiaga R., Lopez-Beceiro, J. and Gracia-Fernandez C. (2013) New method for estimating shift factors in time-temperatura superposition models. Journal of Thermal Analysis and Calorimetry. ISSN 1388-6150. DOI 10.1007/s10973-013-3193-1.

Williams, M. L. (1964) Structural analysis of Viscoelastic materials. AIAA Journal, 785-808.

Zou, J., You F., Su L., Yang Z., Chen G. and Guo S. (2011). Failure Mechanism of Time-Temperature Superposition for Poly(vinyl chloride)/Dioctylphthalate (100/70) System. DOI 10.1002/app.35113.

Ferry J.D. (1980) Viscoelastic Properties of Polymers, Wiley: New York.

Artiaga R., Garcia A. Fundamentals of DMA. In: 'Thermal analysis. Fundamentals and applications to material characterization' (ed.: Artiaga R.) Publicaciones de la Universidade da Coruna, A Coruna, Spain, 183-206 (2005).

Chartoff R.P., Menczel J.D., Dillman S.H. Dynamic mechanical analysis (DMA). In: 'Thermal analysis of polymers. Fundamentals and applications' (eds.: Menczel J.D., Prime R.B.) Wiley, San Jose, 387-496 (2009).

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`PC` *Dataset obtained from polycarbonate (polymer) tests using Dynamic Mechanical Analysis (DMA)*

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### Description

PC contains 49 rows and 3 columns.

### Format

This data frame is composed of the following columns:

`log10.frequency` It accounts for seven different frequencies (rad/s) in logarithmic scale for each temperature (overall 49).

`log10.module` It accounts for seven different storage modulus, E' (Pa), in base-ten logarithmic scale for each temperature (overall 49).

`temperature` Seven different temperaturas: 147, 148, 149, 150, 151, 152, 153 degrees celsius, each one with the corresponding seven values of frequency and storage modulus (overall 49).

### Details

The dataset corresponds to the storage modulus viscoelastic property of different specimens of polycarbonate (PC) and obtained by DMA using TA Instruments Q800 (Naya et al., 2013).

### Source

Naya, S., Meneses A,. Tarrio-Saavedra, J,. Artiaga R., Lopez-Beceiro, J. and Gracia-Fernandez C. (2013) New method for estimating shift factors in time-temperatura superposition models. Journal of Thermal Analysis and Calorimetry. ISSN 1388-6150. DOI 10.1007/s10973-013-3193-1.

### Examples

```
data(PC)
```

# PLOT.TTS — *Time-Temperature Superposition (TTS) plots*

## Description

Plots of TTS results: experimental data, horizontal and vertical shifts, TTS data, TTS Master Curve fitting with B-Splines and bootstrap confidence intervals are deployed.

## Usage

```
PLOT.TTS(x)
```

## Arguments

| | |
|---|---|
| `x` | TTS object. |

## Details

TTS plots are performed from the outputs of TTS function: data, aT, bT, TTS.data, TTS.gam y residuals.

## Value

The following values are returned:

| | |
|---|---|
| `PLOT.data()` | Generic function to plot the experimental data. By default log10.module versus log10.frequency. |
| `PLOT.aT()` | Generic plot of the horizontal shifts corresponding to each curve (modulus versus frequency) obtained on temperature. |
| `PLOT.bT()` | Generic plot of the vertical shifts corresponding to each curve (modulus versus frequency) obtained on temperature. |
| `PLOT.TTS.data()` | Generic plot of the experimental data horizontally and vertically shifted with respect to a the curve corresponding to the reference temperature. |
| `PLOT.TTS.gam()` | Generic plot of the Master Curve B-splines estimation with bootstrap confidence intervals at 95 per cent. |
| `PLOT.res()` | Generic plot of the residuals of Master Curve B-splines fitting. |

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## Examples

```
## TTS object applied to PC dataset.
data(PC)
Derive <- TTS(PC)
x <- Derive
## Generic plots for TTS analysis
PLOT <- PLOT.TTS(x)
names(PLOT)
##[1] "PLOT.data"  "PLOT.aT"   "PLOT.bT"   "PLOT.TTS.data"
##[5] "PLOT.TTS.gam"  "PLOT.res"
## Generic plots of: data, aT, bT, TTS.data, TTS.gam and res
PLOT$PLOT.data(main="PLOT: Data",xlab="log10.Frequency (rad/s)",
               ylab="log10.E'(Pa)")
PLOT$PLOT.aT(main="PLOT: horizontal translation factors",
               xlab="Temperature", ylab="aT")
PLOT$PLOT.bT(main="PLOT: vertical translation factors",
               xlab="Temperature",ylab="bT")
PLOT$PLOT.TTS.data(xlab="log10.Frequency (rad/s)",
               ylab="log10.E'(Pa)")
PLOT$PLOT.TTS.gam( xlab="log10.Frequency (rad/s)",
                ylab = "log10.E'(Pa)",
     main = "Fitted gam, Bootstrap confidence intervals",
     sub = "Reference temperature = 150 degrees celsius")
PLOT$PLOT.res(main="TTS: gam residual", xlab="Fitted",
                 ylab="Standardized residuals")
```

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TTS *Time-Temperature Superposition (TTS) analysis*

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## Description

The Master Curve at a specific temperature is estimated using Time-Temperature Superposition (TTS) procedures. The Master Curve means the variation of a specific viscoelastic property of the selected material depending on time or frequency. TTS procedures provide the viscoelastic property variation at the selected temperature in a wider interval of time or frequency than in the experimental case. The Master Curve is estimated for each selected reference temperaure using TTS procedures. Three TTS methodologies are implemented in this package: the two wider used methods, Arrhenius based methods and WLF, and the newer methodology based on derivatives procedure. The Master Curve is smoothed by B-splines basis.

### Usage

```
TTS(x, reference.temperature = 150, n = 100, nB = 100,
  method = c("derived", "WLF", "Arrhenius"))
```

### Arguments

`x` Matrix or data frame composed of three columns: a numeric column vector with the experimental frequencies (in logarithmic scale, base-ten), the modulus (E' or G') base-ten logarithm vector and, finally the corresponding temperatures vector.

`reference.temperature` Value of the selected reference temperatura at which the Master Curve of modulus will be obtained, the default value of temperature is 150.

`n` Number of partitions in the frequency domain in order to fit the B-spline basis. The default value is 100.

`nB` Number of bootstrap replicates to estimate confidence intervals of master curve fitting. The default is 100.

`method` A string vector composed of one of the following options: "derived" (by default), "WLF" and "Arrhenius".

### Details

El New method for estimating shift factors in time-temperatura superposition models (Naya et al., 2013) opens the possibility to perform the TTS function. The horizontal and vertical shifts are calculated. Namely, the different methods are differenciated due to the expression for estimating the horizontal shifts, aT. The "derivated" method is based on the application of horizontal shifts to the moduli derivatives (depending on the frequency) and thus obtaining the Master Curve at the selected temperature:

(dE')/dx(x+aT) -> (dE')/dx(x)

WLF method is defined by the parametric expression:

Log10(aT)=-C1*(T-To)/(C2+(T-To))

Where C1 and C2 are constants to be estimated, T is the temperature and To the reference temperature.

Arrhenius method is defined by the parametric expression:

Log10(aT)=Ea*((1/T)-(1/To))*log10(2.718282)/R

Where Ea is the activation energy, R = 8.314 J/mol is the universal gas constant, T is the absolute temperature (Kelvin degrees), and To the reference temperature (Celsius degrees).

The vertical shifts, bT, are calculated taking into account the vertical distance between the moduli curves.

## Value

The function returns a list composed of the following outputs:

| | |
|---|---|
| `data` | Input experimental data. |
| `aT` | Numerical vector of horizontal shifts between the modulus curves. |
| `bT` | Numerical vector of vertical shifts between the modulus curves. |
| `TTS.data` | Master Curve Data frame defined by three columns: log10frequency, log10module and temperature. |
| `ref.temp` | Reference temperature value. |
| `TTS.gam` | Data frame of the Generalized Additive Model with B-splines (GAM) estimate of the Master Curve. It contains two columns: frequency and Prediction. |
| `I.lower` | Lower limit of bootstrap confidence interval corresponding to the estimated B-splines Master Curve. |
| `I.upper` | Upper limit of bootstrap confidence interval corresponding to the estimated B-splines Master Curve. |
| `residuals` | Residuals corresponding to the GAM with B-splines Master Curve fitting. |

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### Examples

```
## Polycarbonate dataset
data(PC)
x <- PC
## TTS function applied to polycarbonate.
derive <- TTS(x,reference.temperature=150, method=c("derived","WLF",
              "Arrhenius"))
names(derive)
##[1] "data"    "aT"   "bT"  "TTS.data"  "ref.temp"  "TTS.gam"
##[7] "I.lower"   "I.upper"   "residuals"
## Horizontal shifts vector of modulus versus frequency curves.
derive$aT
## Reference temperature
derive$ref.temp
```

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