Quentin C. P. Bourgogne, Vanessa Bouchart and Pierre Chevrier

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Short paper / Note

On the physical interpretation of pseudo-plastic behaviour of polymers and prediction for various environmental conditions

Quentin C. P. Bourgogne⁎, a, Vanessa Bouchart⁎ a and Pierre Chevriera

a Université de Lorraine, CNRS, ENIM, LEM3, F-57000, Metz, France
URL: https://www.researchgate.net/profile/Quentin-Bourgogne-2
E-mails: quentin.bourgogne@univ-lorraine.fr (Q. C. P. Bourgogne), vanessa.bouchart@univ-lorraine.fr (V. Bouchart), pierre.chevrier@univ-lorraine.fr (P. Chevrier)

Abstract. This paper reports the development of a theory allowing the prediction of the uniaxial mechanical behaviour of thermoplastics as a function of temperature and liquid absorption. This theory takes into account the influence of glass transition temperature and relies on physical phenomena like damage accumulation and molecular-chain motion in order to provide a better understanding of the microstructure changes during the solicitation and their influence on mechanical properties. The theory was validated on a neat polyphenylene sulfide (PPS) and provided good predictions and correlations with experimental data for every environmental configuration studied.

Keywords. Polymers, Modelling, Temperature, Ageing, Glass transition, Damage, Molecular-chain network.

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1. Introduction

Environmental issues are one of the main issues to take into account for new industrial developments. For car manufacturers, for example, one of the main focuses of the CO2 reduction strategy is to reduce the weight of structures, especially by replacing metallic parts by plastic composites. The use of short fibre reinforced thermoplastics is thus widely increasing even for under-the-hood applications. Those applications represent technical challenges as the parts are subjected to temperatures up to 130 °C and are fully immersed in cooling liquid when those parts are activated. The understanding of the mechanical behaviour of those materials is therefore essential in order to design mechanical parts. Many authors worked on the analytical modelling of the mechanical behaviour of these materials in order to be able to make predictions about the evolution of their mechanical behaviour over a wide range of temperatures [1–6]. However,
most of the developed models are restrained to a defined range of temperatures as these materials are subjected to the influence of the glass transition temperature, which is a reference temperature proper to each material. This temperature leading to a complete reorganization of the microstructure, the mechanical properties are highly impacted. Hence, most of the analytical models dealing with the prediction of the mechanical behaviour of polymer-based materials are valid for a defined range of temperatures exclusively under or above the glass transition one [4–6].

Moreover, most of the existing models dealing with non-linear mechanical behaviour are using formalisms developed in metals sciences as concepts like plasticity or viscoplasticity are used to model non-linear behaviour [4, 5, 7, 8]. Even if the results presented in these studies are accurate, those good results are obtained in exchange of a loss of physical representativity as no evolution of grain boundaries are occurring in polymer microstructure. The aim of this study is to investigate the link between the kinetic equations and the polymer physic and give another formalism of the kinematic equations in adequation with the known physical phenomena. From a fundamental and applicative point of view, the exact consideration of the physical phenomena occurring in the material is essential in order to make reliable predictions for complex configurations of solicitation.

Consequently, this paper presents the development and the validation of a theory relying on physical phenomena experimentally observed, such as damage accumulation and evolution of microstructure induced by the molecular network reorganization, based on theories developed for hyperelastic materials [9–12]. Formalisms describing hyperelastic materials and soft polymers behaviours are adapted and used in this theory because they can help to understand the dynamic of change of microstructure occurring in the solicited material and think about the physical meaning of concepts like viscoelasticity and viscoplasticity. Indeed, what is viscosity if it is not a consequence of molecular-chain motion? Take the molecular-chain motion into account hence helps the understanding of those concepts from the point of view of the microstructure of the material. One of the aims of the proposed theory is thus to discuss about the identification of the nature of the physical phenomena leading to the evolution of the mechanical behaviour as a function of strain and study the evolution of these phenomena for various environmental conditions.

This theory also allows prediction of the mechanical properties of the studied material as a function of temperature and liquid absorption and was validated on a neat polyphenylene sulfide (PPS), using a continuum framework valid for temperatures under and above the glass transition temperature, contrary to other developed models. The use of molecular-chain motion contribution, adapted from hyperelastic materials modelling, is taken into account to represent the effects of temperature on the microstructure of the material. Indeed, even if this contribution is low at the ambient temperature, the strain at break of thermoplastics is increasing when the temperature of solicitation increases, leading to tensile curves quite similar to the representative curves of hyperelastic materials as temperature increases the molecular-chain mobility.

The first section of the paper presents the unified theory of prediction of elastic and viscoelastic parameters as a function of temperature and ageing. The developed dependence on temperature is then applied to parameters defining the accumulation of damage and molecular-chain motion. The proposed model is then applied and validated on a neat PPS in Section 3, starting from the ambient temperature to 150 °C, and was also applied on the aged PPS. Finally, a comparative study of the evolution of accumulated damage for each configuration studied showed the influence of viscosity on the mechanical properties.
2. Modelling formulation

2.1. Definition

2.1.1. Evolution of stiffness as a function of temperature

The mechanical properties of thermoplastics and thermoplastics-based reinforced composites are sensible to temperature. The dependence of the mechanical properties on temperature has already been studied experimentally and theoretically for a wide range of materials [1–6, 13, 14]. Recently, a proposition of modelling of the dependence of the mechanical constants of such materials on temperature was defined by the introduction of Arrhenius-type parameters [4, 5]. This dependence allows the prediction of the evolution of the constants, like the Young modulus, for various temperatures and is defined by (1):

$$E(T_{eq}) = E(T_0)e^\delta e \left(1 - \frac{T_{eq}}{T_0}\right),$$

(1)

where $T_0$ is an arbitrary reference temperature, $E(T_0)$ is the Young Modulus at the reference temperature, $T_{eq}$ is the solicitation temperature considering water absorption as defined in (4), and $\delta e$ is an Arrhenius-type parameter allowing the prediction of elastic behaviour through temperature.

It was shown that this model provides very good results, thanks to only two tensile curves obtained at two different temperatures [4, 5]. The weakness of this model is the same as the one of most other studied models dealing with these aspects over a wide range of temperatures and presented in the references. Indeed, the computed Arrhenius-type parameter is valid for temperatures strictly under or strictly above the glass transition temperature. The glass transition temperature being the intrinsic reference temperature of the material, many microstructural changes occur around this temperature. The drastic evolution of the microstructure leads to a brutal change of the mechanical properties so that the models cannot report on the discontinuity between the mechanical behaviours of the material for temperatures under and above glass transition temperature with the same parameters.

A unified theory of the evolution, the mechanical constants as a function of temperature, from under to above the glass transition temperature is proposed by completing the dependence described by (1) with the introduction of a Langevin function. This function is generally used in polymer science to model the hardening observed when the molecular chains align themselves with the direction of solicitation. This function independent of any physical phenomenon and application has an evolution which is appropriate to describe the evolution of the Young modulus as a function of temperature considering the glass transition influence. This function is thus implemented to take into account the influence of glass transition on the loss of stiffness. The dependence of mechanical constants such as the Young modulus on temperature is then described by (2):

$$E(T) = Ye^\delta e \left(1 - \frac{T_{eq}}{T_0}\right) \left(1 - \frac{\gamma T_{eq} - T_g}{T_g} \right),$$

(2)

The variable of the defined Langevin function is dependent of a constant $\gamma$, the glass transition temperature $T_g$, and the temperature of solicitation $T_{eq}$. It is worth noting that no other subjective reference temperature than $T_0$ is defined in the function. This means that this function contains no arbitrary reference and so can be considered as absolute as this function is independent on any kind of references. Indeed, this function is constructed to describe the point of view of the material regarding the temperature influence. Indeed, the only physical reference considering the microstructure of the material being the glass transition temperature, the proposed function considers this temperature as the only real reference. This absolute reference, defining the physical changes within the material without the exterior point of view of the user.
and other arbitrary reference, allows a better description of the influence of temperature on the mechanical properties as it considers the material microstructure as it is, with a mathematical function already used to describe the influence of molecular-chain motion on the macroscopical behaviour of polymers.

From an applicative point of view, however, this means that, in order to describe the evolution of the stiffness as a function of temperature, the knowledge of a tensile curve obtained at a given temperature $T_0$ is still required. As the defined Langevin function is not trivial for a defined reference temperature $T_0$, generally the ambient one, the value of the function for this defined reference temperature must be taken into account to find the experimental Young modulus obtained at $T_0$, such as

$$Y = \frac{E(T_0)}{1 - \mathcal{L} \left( \frac{T - T_g}{T_g} - 1 \right)}, \quad (3)$$

The current temperature $T_{eq}$ is defined as an equivalent temperature in order to describe the influence of liquid or humidity absorption in the same model as a function of mass intake, as described by (4):

$$T_{eq} = T + \xi \frac{wt(\%)-wt_0(\%)}{wt_0(\%)}, \quad (4)$$

where $wt_0(\%)$ is the liquid proportion on a dry-as-moulded material and $wt(\%)$ is the liquid absorption of the aged material.

This equivalence is a generalized version of the one developed in a precedent study conducted on fully immersed materials [4, 5]. This temperature/humidity equivalence is based on experimental study showing the influence of water absorption on the glass transition temperature [3, 15]. This evolution is reported on the current temperature for convenience. Hence, the temperature $T_0$ describes the reference temperature, which was chosen as the ambient one in the precedent studies [4, 5]. $T$ is the temperature of solicitation, and $T_{eq}$ is the equivalent temperature of solicitation of an aged material as a function of liquid absorption. Despite the introduction of the glass transition temperature in the theory, the Arrhenius-type parameter remains defined with respect to an arbitrary reference temperature $T_0$. Consequently, the temperature/humidity equivalence remains attached to the current temperature.

2.1.2. Thermodynamic framework

The complete description of the mechanical behaviour of polymer-based materials is more complex than the definition of the elastic part and its dependences. The aim of this section is to implement the developed method defining the dependence of the stiffness on temperature presented in Section 2.1.1 into a general thermodynamic framework in order to take into account the non-linearity of the mechanical behaviour. Special attention has been paid on the description of physical phenomena occurring in the material when solicited and on the physical signification of the contributions constituting the developed theory, as it was the case in Section 2.1.1.

In most of the developed models dealing with polymer-based materials, plasticity or viscoplasticity formalisms are used to describe the non-linearity of their behaviour. However, conventional parameters like hardening modulus or accumulated plastic strain defining these formalisms, although providing good results, are not representative of the origin of the non-linearity given that what is usually called plasticity in polymer physics differs from the plasticity in metal science.

Consequently, a theory of the mechanical behaviour of polymers is proposed considering viscoelasticity and the modelling of damage accumulation and molecular-chain motion to explain the non-linearity of the mechanical behaviour with a better physical meaning.

A Helmholtz free energy is then defined with two distinct contributions, as presented in (5):

$$\rho \psi = \rho \psi_{\text{vol}} + \rho \psi_{\mathcal{L}}, \quad (5)$$
where \( \rho \psi_{\text{vol}} \) is the volumetric contribution, related to the macroscopic viscoelastic behaviour and a contribution \( \rho \psi_{\xi} \) which is a relaxed contribution.

For uniaxial solicitations, an evolution of the non-linear behaviour of thermoplastic-based materials can be observed on tensile curves obtained at different temperatures [4, 16, 17]. The defined relaxed contribution represents a proposal of explanation of this observation as this contribution defines the irreversible rearrangement of the molecular-chain network, leading to a hardening of the material as a function of strain.

This phenomenon, observed on soft polymers and on rubber [10–12, 17], is used here in order to explain the evolution of the non-linear behaviour of thermoplastics observed when solicited at high temperatures.

The hypothesis made in this paper is that as temperature increases, viscous effects increase, leading to an enhancement of the molecular-chain mobility. This enhanced mobility leads to irreversible changes of the microstructure, a phenomenon which was already observed on SEM micrographs of fracture surfaces of samples solicited at high temperatures [13]. These irreversible changes, which can be observed even on thermoplastics when the temperature of solicitation is high, are responsible for an increase of the maximum strain at break and a hardening of the material. Thus, based on these experimental observations and on the existing relaxed contribution defined on rubbers [9–12], the defined Helmholtz free energy depends on several internal variables as expressed in (6).

\[
\rho \psi (\varepsilon, \varepsilon_{\text{vi}}, T, d) = \rho \psi_{\text{vol}}(\varepsilon, \varepsilon_{\text{vi}}, T, d) + \rho \psi_{\xi}(\varepsilon, \varepsilon_{\text{vi}}, T),
\]

where \( \varepsilon \) is the total strain, \( \varepsilon_{\text{vi}} \) is the viscoelastic strain, \( T \) is the temperature, and \( d \) is damage.

The influence of temperature on the elastic and viscoelastic modulus is taken into consideration. The expression of the volumetric contribution is then defined by

\[
\rho \psi_{\text{vol}}(\varepsilon, \varepsilon_{\text{vi}}, T, d) = \left[ \frac{1}{2} C_\varepsilon^\varepsilon (1 - d)(\varepsilon - \varepsilon_{\text{vi}})^2 + \frac{1}{2} C_{\text{vi}}^\varepsilon (1 - d)\varepsilon_{\text{vi}}^2 \right] \left( 1 - \mathcal{L} \left( \frac{T_{\text{eq}} - T_g}{T_g - 1} \right) \right) \delta \left( \frac{\varepsilon - \varepsilon_{\text{vi}}}{\gamma} \right)
\]

where \( C_\varepsilon^\varepsilon \) is the elastic modulus, \( C_{\text{vi}}^\varepsilon \) is the viscoelastic modulus, \( \varepsilon \) is the overall strain, and \( \varepsilon_{\text{vi}} \) is the viscoelastic strain as defined in the rheological scheme used in the reference studies [4, 5].

The relaxed contribution \( \rho \psi_{\xi} \) is based on the expression used by Guo et al. [9, 10], developed for rubbers. As some microscopic parameters can be hard to determine with precision, this expression is adapted to stiffer materials using macroscopic parameters and their dependence on temperature. The inverse of the used Langevin’s function in the reference study is approximated as a Padé approximation [18], leading to an expression of the relaxed contribution described by (8):

\[
\rho \psi_{\xi} = C_\varepsilon^\varepsilon \left[ \delta \left( 1 - \frac{T_{\text{eq}}}{T_g} \right) \left( 1 - \mathcal{L} \left( \frac{T_{\text{eq}} - T_g}{T_g - 1} \right) \right) \left( \frac{1}{3} \max \left( \frac{\varepsilon - \varepsilon_{\text{vi}} - \varepsilon_y(T)}{x(T)}, 0 \right) \right) \right]
\]

where \( \varepsilon_y(T) \) is the yield strain, that is, the strain representing the start of the accumulation of damage and \( x(T) \) is a coefficient.

As explained at the beginning of this section and as described in the reference study [9], the rearrangement of the molecular network modelled here is assumed irreversible and appearing in the “perfect” network, that is, depending on the purely elastic behaviour of the material. The defined relaxed contribution is thus defined as a function of the elastic modulus \( C_\varepsilon(T) \). This reorganization being irreversible, it also represents a micro-damage system as this reorganization...
does not append without molecular-chain damage [9, 10]. This contribution is thus assumed to start when damage accumulation starts and evolves as a function of the remaining elastic strain in the microstructure.

The combination of the first and the second laws of thermodynamics can be expressed with the 1D Clausius–Duhem inequality defined by (9).

\[
D = \sigma \dot{\varepsilon} - \rho (\psi + s \dot{T}) - \frac{1}{T_0} q_x \text{grad}_x T \geq 0, \tag{9}
\]

where \( \rho \) is the density, \( q_x \) is the heat flux and \( s \) the entropy, which is always non-negative. The derivation of state variables with respect to time is noted \( \dot{X} = dX/dt \).

In order to describe the evolution of internal variables and the viscoelastic dissipation process, a pseudo-dissipation potential is defined as

\[
\varphi(\dot{\varepsilon}_{vi}) = \frac{\tau (C_e^\varphi + C_v^\varphi)}{2} (1 - d) \dot{\varepsilon}_{vi}^2 \tag{10}
\]

with \( \tau \) representing the relaxation time.

Considering the internal state variables of the defined free energy, the derivation of this free energy can be decomposed and implemented in the Clausius–Duhem inequality as follows:

\[
D = \sigma \dot{\varepsilon} - \rho \left( \frac{\partial \psi_{\text{vol}}}{\partial \varepsilon} \dot{T} + \frac{\partial \psi_{\text{vol}}}{\partial \varepsilon} \dot{\varepsilon} + \frac{\partial \psi_{\text{vol}}}{\partial \varepsilon} \dot{\varepsilon}_{vi} \epsilon_{vi} + \frac{\partial \psi_{\text{vol}}}{\partial d} \dot{d} + \frac{\partial \psi_{\text{vol}}}{\partial T} \dot{T} + \frac{\partial \psi_{\text{vol}}}{\partial \varepsilon} \dot{\varepsilon} + \frac{\partial \psi_{\text{vol}}}{\partial \varepsilon} \dot{\varepsilon}_{vi} \epsilon_{vi} + s \dot{T} \right)
\]

\[\quad - \frac{1}{T_0} q_x \text{grad}_x T \geq 0. \tag{11}\]

The state equations of the problem can then be deduced by differentiation of the potential with respect to the state variables:

\[
\sigma = \rho \frac{\partial \psi_{\text{vol}}}{\partial \varepsilon} + \rho \frac{\partial \psi_{\text{vol}}}{\partial \varepsilon} \tag{12}
\]

\[
s = - \frac{\partial \psi_{\text{vol}}}{\partial T} - \frac{\partial \psi_{\text{vol}}}{\partial T} \tag{13}
\]

\[
\rho \frac{\partial \psi_{\text{vol}}}{\partial \varepsilon_{vi}} = - \frac{\partial \varphi(\dot{\varepsilon}_{vi})}{\partial \varepsilon_{vi}}. \tag{14}
\]

As \( (\partial \psi_{\text{vol}}/\partial d) \dot{d} = - \partial \varphi(\dot{\varepsilon}_{vi})/\partial d \), this implies that \( \dot{d} \geq 0 \).

These behaviour laws lead to the general equation (15) allowing the modelling of stress–strain curves considering viscoelasticity, damage accumulation, and molecular-chain motion.

\[
\sigma(\varepsilon, \varepsilon_{vi}, T, d) = C_e^\varphi \delta(1 - \frac{T_{eq}}{T_0}) \left( 1 - \mathcal{L} \left( \gamma \frac{T_{eq} - T_g}{T_g} - 1 \right) \right) \left( 1 - d(T) \right) (\varepsilon - \varepsilon_{vi})
\]

\[\quad + \max \left( \frac{\varepsilon - \varepsilon_{vi} - \varepsilon_y(T)}{x(T)}, 0 \right)^2 \frac{3 - \max \left( \frac{\varepsilon - \varepsilon_{vi} - \varepsilon_y(T)}{x(T)}, 0 \right)^2}{1 - \max \left( \frac{\varepsilon - \varepsilon_{vi} - \varepsilon_y(T)}{x(T)}, 0 \right)^2}. \tag{15}\]

The elastic and viscoelastic modulus are not the only parameters dependant on temperature. Indeed, if these parameters evolve as a function of temperature, this evolution has a direct impact on the yield strain. The same dependence on temperature defined on the elastic and viscoelastic modulus is thus also applied on the yield strain, as described by (16).

\[
\varepsilon_y(T) = \varepsilon_y^\varphi (T_0) \delta(1 - \frac{T_{eq}}{T_0}) \left( 1 - \mathcal{L} \left( \gamma \frac{T_{eq} - T_g}{T_g} - 1 \right) \right). \tag{16}\]

As the molecular-chain motion influence on the mechanical behaviour is defined to be more pronounced when the temperature increases, a dependence on temperature is also applied on
the parameter $x(T)$ and is described by (17).

$$x(T) = x_0^L e^{\delta_e (1-T_0)} \left( 1 - \mathcal{L} \left( \gamma \frac{T_{eq} - T_g}{T_g} - 1 \right) \right).$$  \hfill (17)

2.1.3. Damage law

The mechanical behaviour of the studied materials is not fully elastic or viscoelastic. An accumulation of damage is responsible for the non-linearity observed for important strains. Many damage laws were already developed, local or non-local, in order to study the accumulation and propagation of damage in the solicited material [7, 8, 19, 20]. The aim of this study is to study different physical phenomena occurring in a solicited material and their evolution as a function of temperature. Thus, a Weibull's law, which is a widely used non-local and stochastic law is implemented to model the accumulation of damage [20]. The Weibull's law is described by (18):

$$d(T) = 1 - e^{-E(T) \left( \frac{\max(\epsilon^y(T), 0)}{\sigma_0(T)} \right)^{\beta(T)}},$$  \hfill (18)

where $E(T)$ is the Young modulus and $\sigma_0(T)$ and $\beta(T)$ are the parameters defining the Weibull's law. As it is generally the case, it is assumed that damage accumulation does not start at the beginning of the solicitation but starts at a given strain, which is here the already defined yield strain $\epsilon_y(T)$, also function of temperature.

Most of the studies using Weibull's law or dealing with damage are restrained to ambient temperature. This simple law allows a study of the evolution of damage accumulation as a function of temperature, by defining a dependence on temperature for the characteristic Weibull's parameters. This dependence is assumed to be the same as previously defined for the elastic constants. The different parameters are defined by (19)–(21).

$$E(T) = \frac{C_e^{\rho e} C_{vi}^{\rho e}}{C_e^{\rho e} + C_{vi}^{\rho e}} \delta_e (1-T_0) \left( 1 - \mathcal{L} \left( \gamma \frac{T_{eq} - T_g}{T_g} - 1 \right) \right).$$  \hfill (19)

$$\sigma_0(T) = \sigma_0^{\rho e} \delta_e (1-T_0) \left( 1 - \mathcal{L} \left( \gamma \frac{T_{eq} - T_g}{T_g} - 1 \right) \right).$$  \hfill (20)

$$\beta(T) = \beta_0^{\rho e} \delta_e (1-T_0) \left( 1 - \mathcal{L} \left( \gamma \frac{T_{eq} - T_g}{T_g} - 1 \right) \right).$$  \hfill (21)

2.2. Influence of glass transition temperature

The introduction of the Langevin's function to describe the dependence on temperature of the elastic and viscoelastic modulus allows to take the brutal variation of these moduli around the glass transition temperature into account. However, this evolution of these moduli is not sufficient to represent all of the microstructural changes caused by the crossing of the glass transition temperature. Indeed, as it was shown in one of the reference studies [4], above this temperature of reference, there is no purely elastic behaviour. Hence, the proposed theory needs to be adapted for temperatures above the glass transition one.

As no purely elastic behaviour is observed for temperatures above the glass transition temperature, it is assumed that the global strain is fully a viscoelastic strain:

$$\epsilon \equiv \epsilon_{vi}.$$  \hfill (22)

Following the same philosophy and reflection, if no purely elastic behaviour is considered, the criterion defining the start of damage accumulation is also impacted. A coupled reorganization of the network due to solicitation and high temperature leads to a micro-damage accumulation starting directly at the beginning of the solicitation:

$$\epsilon_y = 0.$$  \hfill (23)
Similarly, the general equation defining the evolution of the mechanical stress as a function of strain is equal to the viscoelastic stress, obtained with the development of (14). The Equation (15), valid for temperatures under the glass transition one, simplified itself as no Maximum function is then necessary. Indeed, as stipulate in (22), above the glass transition temperature, the nature of the strain is homogeneous and presumed fully viscoelastic. The modelling of the tensile curve is thus defined by (24):

$$\sigma(\varepsilon_{vi}, T, d) = \sigma_{vi}(\varepsilon_{vi}, T, d) = (1 - d(T)) C_{vi}^\beta \varepsilon_{vi} \delta \varepsilon_{vi} \left[ (1 - T_{eq} \frac{T_{1}}{T_{0}}) \left( 1 - \lambda \left( \frac{T_{eq} - T_{g}}{T_{g}} - 1 \right) \right) \right]$$

$$\times \left( 1 - e^{-\varepsilon_{vi} \delta \varepsilon_{vi} \left( 1 - T_{eq} \frac{T_{1}}{T_{0}} \right)} \right).$$  \hspace{1cm} (24)

Another difference between (15) and (24) is the consideration of the molecular-chain motion. It can be assumed that above glass transition, the network rearrangement is much more pronounced than the one occurring at lower temperatures. However, as it was modelled in the proposed theory, the modelized molecular-chain motion cannot be taken into account for temperatures higher than the glass transition temperature. The modelled molecular-chain motion represents the irreversible modifications of the network from the point of view of a “perfect” network, that is, the network of the material as it is at ambient temperature exhibiting a purely elastic behaviour. As no perfect network remains at temperatures higher than the glass temperature one, no influence of molecular-chain motion contribution as it was defined can be considered. Indeed, the irreversible modification of the microstructure modelled in this paper is the function of the elastic part of the material, and no elastic part is considered for materials solicited above the glass transition temperature. However, it does not mean that, in reality, there is no influence of the network rearrangement as this reorganization is even more pronounced. This means that this rearrangement is induced by the glass transition and not by the strain imposed by the solicitation. The modelled network rearrangement, however, is the one induced by the solicitation. This is thus not the same physical phenomenon, as the rearrangement of the network induced by the glass transition can occur even when the material is not solicited.

Considering the modifications of the theory and the absence of the defined molecular-chain motion, the Weibull’s parameters need to be redefined for temperatures above the glass transition one, such as

$$\sigma_0 = \sigma_0(T_1)$$ \hspace{1cm} (25)

$$\beta(T) = \beta(T_1) e^{\delta \varepsilon \left( 1 - T_{eq} \frac{T_{1}}{T_{0}} \right)},$$ \hspace{1cm} (26)

where $T_1$ is another arbitrary temperature of reference, above the glass transition temperature.

As the mechanical properties of polymer-based materials solicited above the glass transition temperature are low, the parameter $\beta$ is the only parameter defining the Weibull’s law considered as function of temperature.

3. Application to a neat PPS

3.1. Prediction of the mechanical behaviour for several temperatures and water content

3.1.1. Stiffness prediction as a function of temperature

The proposed theory was applied and validated on experimental data of a neat PPS taken from the reference study [4].
Figure 1. Prediction of the stiffness as a function of temperature and comparison with experimental data [4].

Table 1. Used temperatures for the determination of parameters allowing the prediction of the stiffness as a function of temperature

| Temperatures needed | $T_0$ | Temperature under $T_g$ | $T_1$ |
|---------------------|-------|-------------------------|-------|
| Temperatures chosen | 23 °C | 50 °C                   | 110 °C|

Table 2. Parameters allowing the prediction of the stiffness as a function of temperature

| $Y$ (MPa) | $\delta_e$ | $\gamma$ |
|-----------|------------|----------|
| 1675      | 1.75       | 67       |

The unified theory of the evolution of the stiffness as a function of temperature was first validated. In order to determine the parameters of the proposed model, three tensile curves are required. A first tensile curve at ambient temperature $T_0$ to determine the parameter $\frac{C_v^L}{C_v^L} / C_v^L + C_v^L$, also called $Y$ in Section 2.1.1, meaning the equivalent Young modulus at ambient temperature considering the Langevin's function value at $T_0$. A tensile curve obtained at another temperature under the glass transition temperature is also required in order to determine the parameters $\delta_e$ and a last tensile curve, obtained at a temperature of reference $T_1$, above the glass transition temperature, is used to compute the coefficient $\gamma$.

For the prediction of the stiffness and the entire tensile curves, the three tensile curves used for the determination of the parameters are the ones obtained at the temperatures presented in Table 1.

The last temperature needed is the glass transition temperature of the PPS, which is about 95 °C [4].

The required parameters defining the proposed model are listed in Table 2.

The results of the predicted evolution of the stiffness of the PPS as a function of temperature are presented in Figure 1.

As presented in Figure 1, the proposed model provides very good correlations for every studied temperature and needs only three tensile curves in order to be able to predict the stiffness at any other wanted temperature. The use of the Langevin's function provides a continuum formulation over a wide range of temperatures and models with accuracy the influence of the glass transition on the stiffness of the material.
Figure 2. Experimental data [4] and modelling of the tensile curve of the neat PPS at ambient temperature.

Table 3. Parameters allowing the modelling of the tensile curve of the neat PPS at ambient temperature

| Parameter | Value (MPa) |
|-----------|-------------|
| $C_L^e$  | 3350        |
| $C_L^{vi}$ | 3350       |
| $\beta_0^e$ | 0.66       |
| $\sigma_0^e$ | 55         |
| $\varepsilon_y^e$ | 0.0085   |
| $x_0^{\varepsilon}$ | 1.35     |

As also shown in Figure 1, the use of the Langevin’s function only is not sufficient to describe the entire dynamic of evolution. Indeed, the exponential function defined by the Arrhenius-type parameter is also required to reach an acceptable accuracy of the prediction of the stiffness at temperatures under the glass transition one.

3.1.2. Prediction of entire tensile curves considering damage and molecular-chain motion

Starting from the prediction of the stiffness of the material, this work was applied on the entire tensile curve considering the influence of damage accumulation and hardening induced molecular-chain motion. The tensile curves used to determine the other parameters are the same than the ones used in Section 3.1.1.

Thus, the tensile curve obtained at 23 °C was used to identify the damage parameters listed in Table 3.

The parameter $\varepsilon_y(T_0)$ is directly identified on the tensile curve and the corresponding parameter $\varepsilon_y^e(T_0)$ is then computed considering the value of the Langevin’s function at $T_0$. The parameters $C_L^e$ and $C_L^{vi}$ are directly deduced from the macroscopical stiffness listed in Table 2 with the Newton–Raphson method. The difficulty was to determine two parameters with one value of stiffness. In order to do so, an artificial intelligence algorithm was used and coupled to the Newton–Raphson algorithm in order to determine values of the parameters $C_L^e$ and $C_L^{vi}$. The presented model was solved with the Mathematica© software, with the overall strain as an input.

The results of the modelling of the tensile curve at ambient temperature are presented and compared with experimental data [4] in Figure 2.

As shown in Figure 2, the dynamic imposed by the Weibull’s law is particularly adapted as the experimental non-linear behaviour exhibits a form different from a stabilization, which is generally the case when the studied material is a metal. Here, however, the dynamic is characteristic of the probabilistic evolution provided by the Weibull’s law. The study of the different contributions shows that, as expected, the contribution of the molecular-chain motion is negligible. Indeed, at ambient temperature, thermoplastics like PPS do not present an elevated strain at break but are
Figure 3. Experimental data [4] and modelling of the tensile curve of the neat PPS at 50 °C.

considered as stiff, inducing a reduced molecular-chain mobility compared to hyperelastic materials. Moreover, the experimental pseudo-plastic behaviour being characteristic of the accumulation of damage modelled by the Weibull’s law, a negligible molecular-chain motion influence was expected.

The prediction capabilities of the proposed methodology as a function of temperature were then tested for tensile curves obtained at 50 °C and 70 °C. The results of the modelling of the tensile curve at 50 °C are presented and also compared with experimental data in Figure 3.

As shown in Figure 3, the viscoelastic part of the curve is very well predicted. This can be explained by the fact that the curve obtained at 50 °C was used in order to determine the parameter $\delta_e$ and $\gamma$ listed in Table 2. The damage accumulation is fully predicted, thanks to the dependence on temperature of the parameters defined by (20) and (21), as it is also the case for the molecular-chain motion influence and its dependence on temperature defined by (16) and (17).

As shown in Figure 3, as the temperature increases, the strain at break of the solicited material increases, which signifies that the molecular-chain mobility is more pronounced that observed at ambient temperature. This molecular-chain mobility induces an enhanced contribution of the molecular-chain motion and so a hardening compensating the loss of properties due to damage accumulation. This compensation results in the observed stabilization of the pseudo-plastic behaviour observed at temperatures higher than the ambient one.

The pseudo-plastic behaviour is, for this temperature, fully predicted. Even if the defined dependence on temperature of the parameters related to damage and molecular-chain motion is the same as for a macroscopic parameter, the Young modulus, the pseudo-plastic behaviour at 50 °C is predicted with an acceptable accuracy.

The last step of the validation consisted in the prediction of an entire tensile curve, from the viscoelastic part to the pseudo-plastic part. Indeed, even if the pseudo-plastic part was fully predicted on the curve obtained at 50 °C, the viscoelastic part was used to determine the parameters listed in Table 2.

The complete theory was thus validated at another temperature: 70 °C. The results are presented in Figure 4.

As shown in Figure 4, the model predicts the tensile curve with good accuracy. The viscoelastic part and the pseudo-plastic parts are well predicted.

It can be seen that the non-linear behaviour of the studied materials exhibits a plateau and not a strain hardening as observed in soft materials. However, even if no strain hardening is visible on
the tensile curves, this does not necessarily mean that no reorganization of the network occurs. If it is not visible on the tensile curves, this is because this hardening is compensated by damage accumulation. The modelled damage accumulation and the comparison with the modelled molecular-chain motion influence showed that the first physical phenomenon is preponderant in the mechanical behaviour of the studied material at ambient temperature and equivalent to the network reorganization influence when temperature increases, which is coherent with its semi-crystalline nature.

As also shown in Figure 4, as the yield strain decreases and the strain at break increases with the increase of temperature, the contribution of the molecular-chain motion is more pronounced than at 50 °C. As the experimental and predicted plateau of the non-linear behaviour and its ultimate strain becomes more important, meaning that the hardening due to molecular-chain motion compensates equivalently the loss of properties due to damage, the behaviour of this thermoplastic shows some similarities to the behaviour of softer polymers and hyperplastic materials [12, 17] as the molecular-chain mobility influence increases. Moreover, the hardening induced by the molecular-chain motion is defining, as it was modelled, irreversible changes of the microstructure. Hence, if the proposed theory is correct, the microstructure of a thermoplastic solicited at high temperature must be different from the one observed at ambient temperature.

Observations with SEM of the fracture surface of this kind of materials solicited at different temperatures were already performed by Eftekhari et al. [13] and showed differences of the microstructure on the fracture surfaces. The surface microstructure of the material solicited at ambient temperature presented a microstructure characteristic of a fragile fracture while the surface microstructure of the material solicited at high temperature was characteristic of a ductile fracture. As the observations were performed at ambient temperature, after the tensile tests, the observed microstructure of the material solicited at high temperature remained the same as it was when solicited, meaning that this change of microstructure is irreversible. Consequently, the hypothesis made in this paper that there is an important contribution of irreversible changes in the material network when the temperature of solicitation is high is in accordance with previous experimental observations.

As it was the case in the reference study [4], this work can also be applied on aged materials, thanks to a temperature/absorption equivalence defined by (4) and function of the mass intake. The proposed model was then applied on a PPS which absorbed water at saturation. The parameters linked to the ageing configuration are listed in Table 4.

The results of the extrapolation of the proposed model on the aged PPS containing 0.3% of water are presented in Figure 5.

Figure 4. Experimental data [4] and modelling of the tensile curve of the neat PPS at 70 °C.
Figure 5. Experimental data [4] and modelling of the tensile curve of the aged PPS with 0.3% of water.

Table 4. Parameters allowing the modelling of the tensile curve of the aged PPS

| $\xi$ | $\omega t$ (%) | $\omega t_0$ (%) |
|-------|----------------|------------------|
| −0.22 | 0.3            | 0.01             |

As shown in Figure 5, the prediction of the proposed model is very accurate, validating the pertinence of the defined temperature/absorption equivalence and the good prediction capabilities of the proposed model as a function of temperature.

As also shown in Figure 5, the aged configuration looks like the ambient temperature condition as a slight increase of the stiffness was observed due to the temperature of ageing [21–23]. As the strain at break decreased after the ageing process, the molecular-chain motion contribution is negligible, as it was also the case at ambient temperature. In this case, an irreversible change of microstructure is, however, possible due to the insertion of water molecules in the molecular network. This rearrangement represents a physical phenomenon which is not taken into account in the theory, as it is the case for the influence of the glass transition on the microstructure, as the irreversible network modification due to ageing is happening even without any mechanical solicitation.

Indeed, the molecular-chain motion contribution modelled in this paper is related to the solicitation and function of the strain of the material coupled to the environmental condition. The theory does not take into account the influence of the temperature and/or water absorption on the microstructure decoupled from the solicitation type as this theory is purely mechanical. Consequently, the profound variation of the microstructure due to the glass transition required an adaptation of the proposed model, which was presented in Section 2.2.

The parameters defining the Weibull’s law above the glass transition temperature and the damping parameter are listed in Table 5. The other needed parameters remain the same as those listed in Tables 2 and 3.

The parameters listed in Table 5 are identified with the tensile curve obtained at the last required temperature $T_1$, the defined temperature of reference above the glass transition temperature. The results of the modelling of the tensile curve obtained at 110 °C are presented in Figure 6.

As shown in Figure 6, the viscoelastic part is well modelled by the Langevin’s function and the new parameters of the Weibull’s law suit well the dynamic of the curve. This result was expected as the tensile curve obtained at 110 °C was used in order to identify some of the
Figure 6. Experimental data [4] and modelling of the tensile curve of the neat PPS at 110 °C.

Table 5. Influence of glass transition on the Weibull's law parameters

| β(T) | σ0(T) (MPa) | τ (s) |
|------|-------------|-------|
| 0.42 | 18          | 10    |

parameters. All required parameters for temperatures above the glass transition temperature are thus determined.

Finally, the adaptation of the proposed model for tensile curves obtained at temperatures above the glass transition one was validated with experimental data obtained at 130 °C and 150 °C.

The fully predicted tensile curves at 130 °C and 150 °C and the comparison with experimental data are presented in Figure 7.

As shown in Figure 7, the predicted curves are in accordance with the experimental data. The proposed theory is thus also reliable for temperatures higher than the glass transition temperature. The main strength of the developed theory is that it provides the prediction of the tensile curves of polymers for a wide range of temperatures, including the consequences of glass transition and ageing, in a continuum framework. The modelling of phenomena like damage and molecular-chain motion provides a modelling more in accordance with the reality than the formalisms used in metal science and so, in accordance with experimental observations [4, 13]. A representative theory of the reality allows a better understanding of the evolution and the influence of the physical phenomena occurring in a solicited material on its mechanical properties. This understanding is a fundamental step in order to extend and refine predictions of the mechanical behaviour of such materials solicited in various and complex configurations. The proposed theory is hybrid as it is based on macroscopic parameters like elastic and viscoelastic modulus and their dependence on temperature to define microscopic phenomena and their evolutions. This hybrid point of view allows an easy identification of the parameters and a theory easily usable in an industrial context, as the theory only needs three tensile curves to be able to predict all other curves at any wanted temperature.

Even if the prediction capabilities of the developed model are acceptable, it can be improved. Indeed, even if it is convenient to reuse the dependence on temperature of mechanical constants for molecular-chain motion and damage related parameters, an intrinsic dependence on temperature of each physical phenomenon would be interesting from a fundamental point of view.
Figure 7. Experimental data [4] and modelling of the tensile curve of the neat PPS at (a) 130 °C and (b) 150 °C.

Nevertheless, the developed theory can represent the basis of multi-scale analyses and simulations in order to extend this work to reinforced composites as phenomena like damage can thus be studied in a local way on composites over a wide range of environmental conditions and thus extend the recent multi-scale models [24–27].

3.2. Comparative study of the accumulated damage for different environmental conditions

As the proposed model takes the damage accumulation during the solicitation into account, a comparative study of damage evolution for different environmental configurations was performed. The evolution of damage accumulation for the studied cases is presented in Figure 8.

As presented in Figure 8(a), the configuration of a solicitation at 70 °C represents the solicitation where the damage accumulation is the most pronounced. This accumulation increases when the temperature increases. The aged condition, modelled as equivalent to a temperature of solicitation slightly lower than the ambient one, provides the smallest damage accumulation.
This particular result does not necessarily mean that there is less damage in aged materials. The damage accumulation, as it was modelled, can be interpreted as an irreversible modification of the microstructure, as for the molecular-chain motion consequences. Hence, this result signifies that the more the damage accumulation is pronounced, the more the microstructure is affected. The microstructure of the material solicited at 70 °C is thus the most affected, leading to a fracture surface microstructure considered as ductile, while the aged material one is brittle, as its microstructure is not globally affected. This result and this interpretation are fully in accordance with the SEM observations [13]. It is worth noting that, for a same strain, the damage accumulation at high temperature is more pronounced, thanks to a yield strain, among the other parameters, which is also dependant on temperature. This yield strain being dependant on the temperature, the higher the temperature of solicitation is, the sooner the damage accumulation starts. The shape of the dynamic of accumulation also varies as a function of the temperature. Indeed, the accumulated damage at 70 °C is more important than the one at 23 °C right after the
yield strain. This can be explained by the defined dependence on temperature of the Weibull’s law parameters.

In Figure 8(b), a completely different dynamic than the one obtained in Figure 8(a) can be observed. Indeed, as the theory was adapted for temperatures above the glass transition one, the Weibull’s law parameters and their dependence were also adapted. This adaptation leads to a damage accumulation more pronounced for lower temperatures. It is difficult to say without any doubt if this result is in line with experimental observations. For temperatures higher than the glass transition one, viscosity is the physical phenomenon leading to the mechanical behaviour of the material [4]. Thus, as non-linear viscoelasticity can be considered as a reversible physical phenomenon, then the dynamic presented in Figure 8(b) can be interpreted as an indication on the influence of viscosity on the mechanical behaviour of such materials. Indeed, as damage accumulation decreases when temperature increases, this would mean that viscosity is the main responsible for the decrease of the mechanical properties as a function of temperature, when the temperature is above the glass transition one.

The developed theory was built as a legislative solution, based on experimental observations and formalisms used to describe the microstructure modification of a solicited material from the point of view of the molecular chains. Hence, this theoretical study is in accordance with experiments, at least for temperatures under the glass transition temperature. Above this temperature, even if the prediction capabilities of the theory remain satisfying, it is difficult to experimentally identify with precision the preponderance of the physical phenomenon leading to the obtained mechanical behaviour. As it was modelled, the developed theory proposes an answer to this question, as the viscosity is defined as the main responsible for the decrease of the mechanical properties for this range of temperatures. This last point represents an axe of experimental investigation in order to confirm or disprove this hypothesis and refine the theory above the glass transition temperature. An enhancement of the damage accumulation law would be an improvement in order to model cyclic tests as it was the case in a precedent study [28]. Finally, an extension of this word in 3D would be suitable in order to implement it in a Finite Element code coupled with SEM observations to study the damage mechanisms and enhance the used laws.

4. Conclusion

This paper reports the development and the validation of a new theory describing the uniaxial non-linear mechanical behaviour of thermoplastics. The proposed model was developed in order to take into account observed physical phenomena and free the used formalism from plasticity and viscoplasticity concepts, as the physical meaning of those concepts are only adapted to metal science. Hence, the proposed methodology is based on damage accumulation and molecular-chain motion, which is a formalism based on existing and realistic modelling of hyperelastic materials. The developed theory uses macroscopic and microscopic parameters and defines an easy-to-use unique dependence on temperature for all parameters considered to be sensible to temperature. The theory was validated on a neat PPS and showed good predictions of the tensile curves of the material as a function of temperature. This dependence on temperature is defined, contrary to most of the existing models, in a continuum framework, taking into account the influence of glass transition temperature. The definition of a temperature/absorption equivalence allowed the prediction of the tensile curve of an aged PPS. This work showed that damage accumulation and irreversible changes of the microstructures are more pronounced at high temperature, which is in line with previous experimental observations. This work also showed that, above the glass transition temperature, the influence of viscosity on the mechanical properties is higher than the influence of damage accumulation. As the developed model considers macroscopic parameters like Young modulus and the reuse of its dependence on temperature on the
other parameters, this model needs only tensile curves obtained at three different temperatures to be able to predict the tensile curves at any other temperature. Based on physical phenomena, the next step of the development is the extrapolation of this work to the composite level. An implementation of this model in homogenization schemes and/or in finite-element-based simulations, considering local law of damage and reinforcement type, can allow a better study of the damage accumulation and microstructure changes, their evolution as a function of various environmental conditions, and their consequences on the mechanical behaviour of reinforced plastics. The use of the stiffness dependence on temperature on other parameters provides good results and allows the prediction of the tensile curves as a function of temperature with a reduced amount of experimental data, which is adapted for the industrial context. However, from a fundamental point of view, a definition of the dependence on temperature of damage law and molecular-chain motion parameters separately would be interesting to understand the influence of both physical phenomena independently and determine the change of preponderance of each physical phenomenon on the mechanical properties as a function of temperature.

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