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Investigation of temperature-dependent mechanical behaviours of polycarbonate with an innovative fractional order model

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Abstract. Amorphous thermoplastic polymers are considered as essential engineering materials. However, their strongly temperature-dependent elastic-viscoplastic behaviour is still not well understood. The large deformation response of these materials in the temperature range spanning the glass transition temperature is highly required. In this paper, the uniaxial compression tests are performed with large deformation on a polycarbonate amorphous polymer, within a forming temperature range from 60 °C to 180 °C. The variable order fractional constitutive model is improved to describe the evolution of mechanical behaviour of polycarbonate at different temperatures. The fractional order in the model is proposed as a function of time. The simulation results are in good agreement with the experimental data. It is concluded that the variable order fractional model is an efficient tool to predict the large deformation of amorphous polymers under different temperatures.

Introduction

Polycarbonate (PC) exhibits excellent mechanical, chemical and physical properties such as transparency, toughness, ductility and elasticity, making it widely used as a structural material [1]. However, significant influences of temperature are observed on its physical properties, such as color changes, surface cracking and mass loss [2]. It is necessary to propose an effective constitutive behaviour law to accurately describe its mechanical properties due to the strong dependence on temperature.

The mechanical behaviour of PC is greatly changed above its glass transition temperature (Tg). It behaves as a rubbery phase with a viscoelastic response. Below Tg, strain softening occurs before strain hardening, and it behaves as a glassy phase [3]. Over the past few decades, many constitutive models have been developed to describe the complex behaviour of polymers considering the glass transition [4-7]. Alves et al. [8] proposed a constitutive model for the deformation behaviour of PC below Tg. These constitutive models usually require a considerable number of parameters to identify the characteristics of polymers due to their complex temperature-dependent behaviours [9,10]. Temperature has a great impact on rheological property of PC during the forming process [11,12]. In order to simulate these manufacturing processes with fewer material parameters, an accurate and efficient constitutive model is still strongly required in a wide temperature range.

A variable order fractional (VOF) derivative operator is introduced into the viscoelastic model to improve its accuracy and reduce the number of identified parameters. The order of fractional derivative is supposed to be a function of the independent variable (time or space) [13]. It provides a new way to describe the time dependence and historical memory of viscoelastic materials. Based on the molecular chain conflict theory, Meng et al. [14] verified that the corresponding mechanical

property evolution revealed by fractional order was reasonable. They demonstrated that the VOF model could effectively describe the compression deformation of amorphous polymers.
In this study, the mechanical behaviours of PC below and above Tg are analyzed numerically and experimentally. A linear function is proposed for the fractional order to simulate the viscoelastic behaviour above Tg. A power function is applied to the fractional order to describe the large deformation of polymer below Tg. The material parameters of the models are identified by inverse method according to the experimental data.

Fractional viscoelastic constitutive model
The VOF model of viscoelasticity is expressed as follows [15]:

$$\sigma(t) = E\theta^{\alpha(t)} D_t^{\alpha(t)} \varepsilon(t), 0 < \alpha(t) < 1. \tag{1}$$

where $\sigma(t)$ is stress, $\varepsilon(t)$ is strain, E is elastic modulus, $\theta = \eta/E$ is relaxation time, η is viscosity coefficient. $D_t^{\alpha(t)}\varepsilon(t)$ represents VOF derivative of $\varepsilon(t)$, where $\alpha(t)$ is the variable fractional order. When $\alpha(t) = 0$, the model becomes pure elastic behaviour law, represented by a Hookean spring, while $\alpha(t) = 1$, it becomes Newton's law of viscosity, represented by a dashpot. The fractional order is defined between 0 and 1, represents the viscoelastic behaviour of the material. Three parameters E, θ and $\alpha(t)$, need to be identified in VOF, shown in Fig. 1.

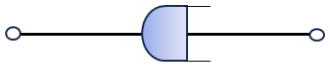

Fig. 1. Schematic of VOF model.

In this study, the VOF differential operator proposed by Ramirez and Coimbra [15] is adopted:

$$D^{\alpha(t)} f(t) = \frac{1}{\Gamma[1-\alpha(t)]} \int_0^t (t-s)^{-\alpha(t)} f(s)^{(1)} ds + \frac{(f(0+)-f(0-))t^{-\alpha(t)}}{\Gamma[1-\alpha(t)]}. \tag{2}$$

where $\Gamma(*) = \int_0^* e^{-s} s^{*-1}\, ds$ is Gamma function, $f(s)^{(1)}ds$ represents the first derivative of $f(s)$ with respect to variable s.
When the deformation rate of the material is constant, its strain can be expressed as follows:

$$\varepsilon(t) = \dot{\varepsilon}\mathrm{t}. \tag{3}$$

where $\dot{\varepsilon}$ is the constant strain rate.
Substituting of the strain rate into Eq. (1) and using the definition of Eq. (2) gives:

$$\sigma(t) = E\theta^{\alpha(t)} \frac{\dot{\varepsilon} t^{1-\alpha(t)}}{\Gamma(2-\alpha(t))}. \tag{4}$$

The equation of VOF stress-strain relationship is obtained:

$$\sigma(t) = E(\dot{\varepsilon}\theta)^{\alpha(t)} \frac{\varepsilon(t)^{1-\alpha(t)}}{\Gamma(2-\alpha(t))}. \tag{5}$$

The fractional order in the VOF model exhibits a linear relationship with strain [16], which is mathematically formulated as $\alpha(\varepsilon) = a\varepsilon + b$, where a and b are constants. Other functions are proposed for the fractional order to describe the complex behaviours with large deformations. Strain-dependent power function $\alpha(\varepsilon) = c\varepsilon^d + e$, where c, d and e are constants, has recently

been proposed to describe complex non-linear stress-strain responses [17]. The model needs to be validated with amorphous thermoplastic polymers. In this study, it is applied to describe the mechanical behaviours of an amorphous polymer and the simulation accuracy is confirmed with experimental data.

Experimental tests and numerical approach

Thermoplastic polymer PC was selected in this study. Injection molding technology was applied to fabricate the cylindrical samples. Uniaxial compression tests were carried on to obtain the stress-strain relationships. Both ends of the PC sample were polished to reduce friction between the polymer and mould. The sample was inserted between two metal plates in an oven. Uniaxial compression tests were repeated several times at different temperatures. Based on the standard ISO 604, a constant strain rate 0.003 s^{-1} was applied during the test and the true strain of the sample was more than 50% [18]. The material parameters in VOF model were identified based on the experimental data with the least squares method, via MATLAB. The effectiveness of the identification was assessed by the values of root mean square error (RMSE) and coefficient of determination (R^2). A flowchart describing the numerical approach is shown in Fig. 2.

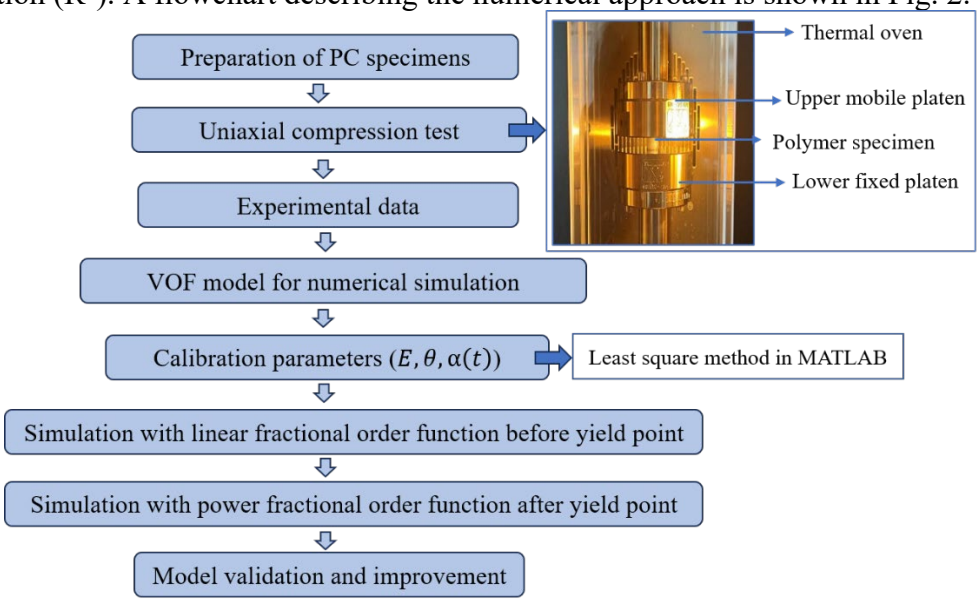

Fig. 2. Flowchart of the general methodology for the identification of material parameters in VOF model.

Results

The compression tests were conducted on PC in the temperature range of 60-180°C, with a Tg approximately 150 °C. Fig. 3 shows the evolution of true stress in function of true strain of PC under different temperatures. For the same true strain, the true stress decreases with temperature. At temperature below Tg (Fig. 3 (a)), the stress-strain curve exhibits an obvious glassy phase, with a strain softening stage after yielding and a strain hardening stage at large strains. At temperature above Tg (Fig. 3 (b)), the yield point and strain softening disappear, but strain hardening still exists. The true stress of PC is significantly reduced and a rubbery phase appears. The true stress tends to increase with true strain at temperature above Tg. PC exhibits different true stress-strain curve at 140 °C and 160 °C, which confirms the glass transition stage in this temperature range.

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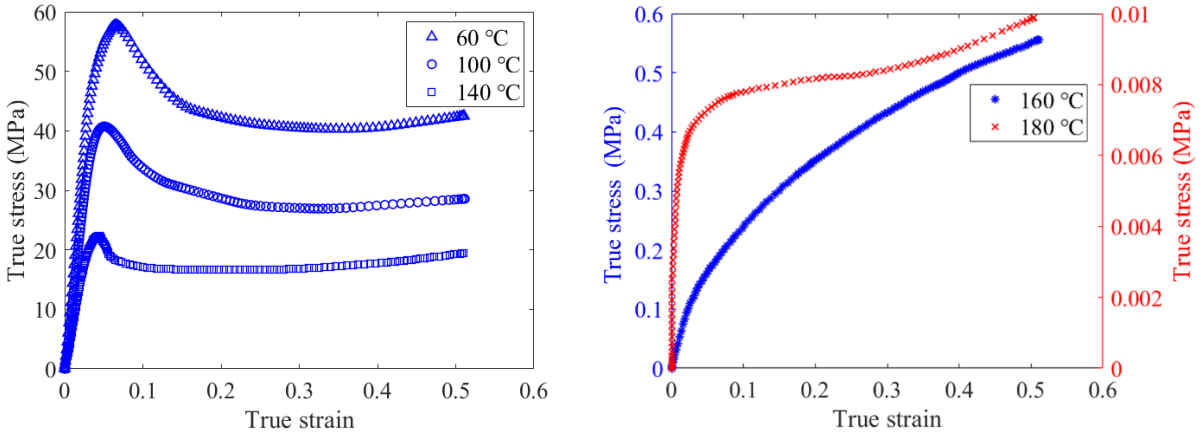

(a) (b)

Fig. 3. True stress-strain curves obtained in uniaxial compression tests of PC at constant strain rate 0.003 s^{-1} across the glass transition (a) below Tg (b) above Tg.

From a physical perspective, the mechanical responses of polymers in glassy and rubbery phase are dominated by intermolecular and intramolecular chain resistance respectively [19]. The glass transition is the critical state where these two mechanisms work together. The evolution of true stress of polymer is greatly affected by temperature. It is difficult to apply the same material model to effectively describe its mechanical behaviour over the entire glass transition range.

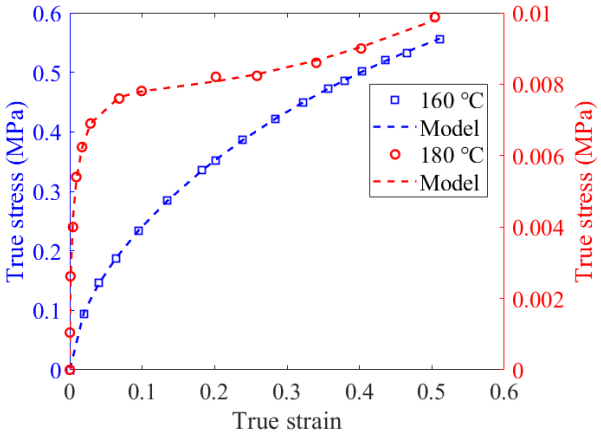

Fig. 4. Comparison of true stress-strain curves between experiment data and model predictions above Tg.

VOF model was proposed to characterize the mechanical behaviour above Tg. A linear function $\alpha(\varepsilon) = a\varepsilon + b$ was proposed for the fractional order, because no obvious yield phenomenon was observed in the true stress-strain curve, shown in Fig.3 (b). The comparisons between the numerical model predictions and experimental data are shown in Fig. 4. It can be observed that the model predictions are in good agreement with the experimental data, which confirms that the VOF model can well fit the stress-strain response of PC at temperatures above Tg. The parameters in the model were identified by using the least squares method. The model parameters are shown in Table 1. The elastic modulus E decreases with temperature and the relaxation time θ increases with temperature. The value of the fractional order increases and is always less than 1. The decrease of fractional order reflects the strain hardening of PC under large deformation. The fractional order possesses a larger value at higher temperature, which indicates that the mechanical behaviour of PC is close to Newton's law.

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Table 1. Identified parameters of VOF model for PC above Tg.

T (°C)	E (MPa)	θ (s)	a	b	RMSE	R^2
160	1.54	68.20	0.14	0.44	0.0016	0.9999
180	0.07	137.11	0.07	0.85	0.000096	0.9989

Fig. 5 (a) shows the PC true stress-strain curve, which is divided into two regions by the yield point. The value of the yield point is obtained according to the experimental data. The VOF model with linear fractional order function is applied to describe the relationship of true stress and strain below Tg. The results are shown in Fig. 5 (a), the experimental data cannot be well fitted by this model. Because the mechanical properties of PC change significantly before and after the yield point. Therefore, it is necessary to propose different fractional order function before and after yield point in this temperature range. A VOF model with linear fractional order function is applied to characterize the mechanical behaviour of PC before yielding, with a power function selected after yielding.

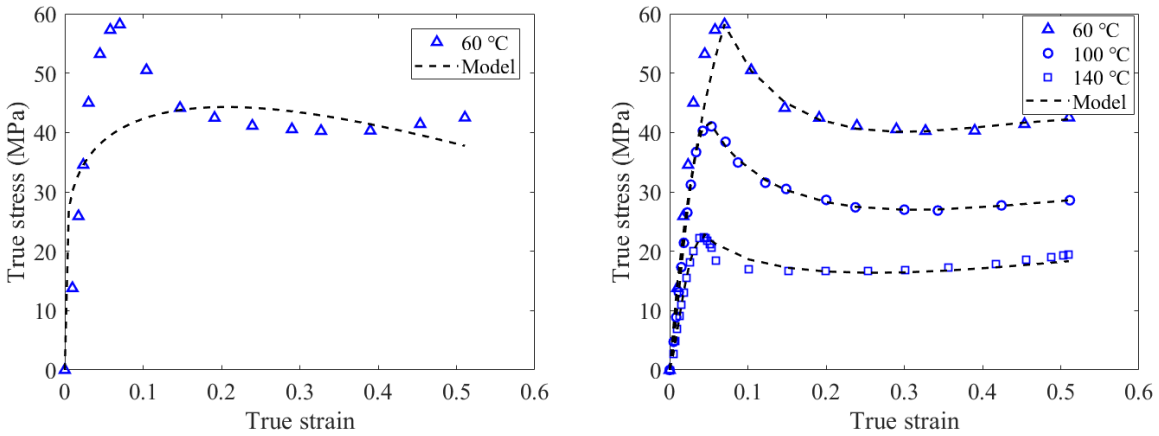

Fig. 5. Identification of true stress-strain curves below Tg by using VOF model with (a) linear fractional order function and (b) linear and power fractional order function.

The two regions of the stress-strain curves are characterised separately. The first region represents viscoelastic deformation, and is described by VOF model with a linear fractional order function $\alpha(\varepsilon) = a\varepsilon + b$. The second region represents non-linear viscoplastic deformation and is described by using a power fractional order function $\alpha(\varepsilon) = c\varepsilon^2 + e$. The two functions were obtained by fitting the experimental data before and after PC yielding with the least squares method. In Fig. 5(b), the proposed model accurately fits the experimental data at different temperatures below Tg. The evolution of fractional order in function of true strain at different temperatures below Tg is shown in Fig. 6. In the viscoelastic and viscoplastic deformation stage, the fractional order increases with temperature. VOF models with various fractional order functions are quite efficient to characterize the mechanical properties below Tg.

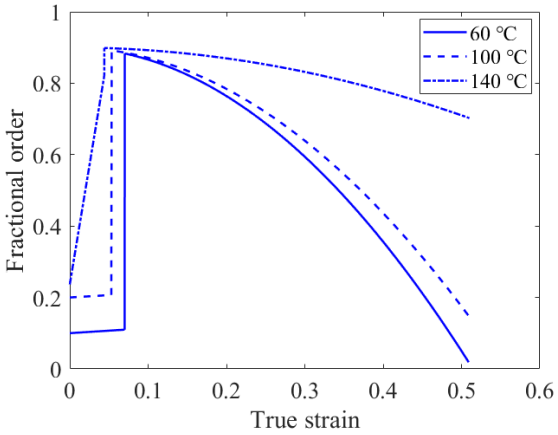

Fig. 6. Evolution of fractional order vs. true strain at different temperatures below Tg.

Based on Fig. 6, the linear and power fractional order functions are continuous at the yield point for each temperature. The linear function increases with strain before the yield point, followed by the power function that decreases after the yield point. The fractional order varies between 0 and 1 during the viscoelastic and viscoplastic deformation stage, satisfying the definition of variable fractional order. The evolution of mechanical property is accurately described by using a fractional constitutive behaviour law. The variable fractional order is expressed by a piecewise function, consisted of a linear and power fractional order function. The numerical simulation results are consistent with the existing experimental research [20], the viscoplastic response of materials is strongly affected by the yield stress, strain rate, and temperature.

Conclusions

In this study, the VOF model was proposed to describe the mechanical behaviours of amorphous polymer across a wide temperature range (below and above Tg). Compression experimental data were used to identify the material parameters and validate the accuracy of the proposed constitutive model. The main conclusions are as follows:

1. The VOF model effectively captures the evolution of mechanical properties of amorphous polymers across Tg.
2. Above Tg, VOF model with a linear fractional order function is suitable to characterize the mechanical behaviours of PC. While below Tg, VOF model with linear and power fractional order function is required.
3. The fractional order increases gradually with temperature, which confirms the efficiency of VOF model in describing the glass transition of amorphous thermoplastic polymer.

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