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CONTENTS

RESEACH ON THE THERMAL-MECHANICAL BEHAVIOUR OF THERMOSET POLYMER COMPOSITES REINFORCED WITH GLASS FIBER

NGHIÊN CỨU ỨNG XỬ CƠ - NHIỆT CỦA VẬT LIỆU COMPOZIT NỀN POLYME NHIỆT RẮN TĂNG CƯỜNG SỢI THỦY TINH

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ABSTRACT

Bulk Molding Compound (BMC) are thermoset polymer composites widely used in electric and automotive industries. In the literature concerning the behaviour of injected thermoset compounds such as BMC is quite scarce. This knowledge is however a key to improve the design of moulds in order to produce parts with better and less contrasted physical and mechanical properties. Hence, the objective of this study consists of the experimental characterization and the modelling of the thermal-mechanical behaviour of BMC during their injection. For that purpose, various BMC formulations with the same polyester resin have been studied, i.e. with three fiber contents (0, 10 and 20 wt%). Cylindrical BMC samples (diameter 110 mm, height 25 mm) were produced and deformed under homogeneous simple compression deformation mode at constant axial strain rates. Experimental results emphasize the influence of the imposed strain rate, the mass fraction of fibers as well as the temperature on the BMC behaviour. An elementary 1D elastoviscoplastic model is then proposed in order to reproduce the observed experimental trends.

TÓM TẮT

BMC là vật liệu compozit nền polyme nhiệt rắn được sử dụng rộng rãi trong công nghiệp điện và ôtô. Các công trình nghiên cứu liên quan đến ứng xử của vật liệu như BMC là rất hiếm. Hiểu rõ điều đó như là một chìa khóa để cải thiện việc thiết kế khuôn để nhận được các sản phẩm tốt hơn và các tính chất cơ lý nổi bật. Chính vì vậy, mục đích của nghiên cứu này bao gồm những đặc trưng thí nghiệm và mô hình hóa ứng xử cơ nhiệt của vật liệu composite nền polyme nhiệt rắn tăng cường bởi sợi thủy tinh trong quá trình tạo hình. Với mục đích đó, thành phần BMC có cùng nhựa polyeste đã được nghiên cứu tương ứng với 0, 10, 20% khối lượng sợi khác nhau. Mẫu BMC có đường kính 110mm, chiều cao 25mm đã được thực hiện dưới biến dạng nén đơn tại các hằng số tốc độ biến dạng khác nhau. Kết quả thí nghiệm làm rõ ảnh hưởng của tốc độ biến dạng, tỷ lệ khối lượng sợi cũng như nhiệt độ đến ứng xử của BMC. Một mô hình ứng xử đàn dẻo nhớt đã được đề xuất để so sánh với các kết quả thí nghiệm.

I. INTRODUCTION

Bulk Moulding Compounds (BMC) are composite materials that are made of a filled thermoset resin reinforced by entangled short glass fibers. They offer a high corrosion resistance and make possible to design parts integrating several functionalities. They are mainly used by the electric industry. Mass production BMC parts are moulded by injection. If the behaviour of thermoplastic polymers reinforced by short fibers has already been quite largely studied, the literature concerning the behaviour of injected thermoset compounds such as BMC is quite scarce, [1]. This knowledge is however a key to improve the design of moulds in order to produce parts with better and less contrasted physical and mechanical properties.

Hence, the objective of this study consists in the experimental characterization and the modelling of the thermal-mechanical behaviour of BMC during their injection. For that purpose, various BMC formulations with the same polyester resin have been studied, i.e. with three fiber contents (0, 10 and 20 wt%). Cylindrical BMC samples (diameters 110 mm, height 25mm) were produced and deformed under homogeneous simple compression deformation mode at constant axial strain rates in section 2. Note that, compression data were corrected in order to account for the influence of the lubrication layer (between samples and rheometer plates) on recorded stress levels, [2]. Experimental results emphasize the influence of the imposed strain rate, the mass fraction of fibers, as well as the temperature on the BMC behaviour in section 3. An elementary 1D elastoviscoplastic model is then proposed in order to reproduce the observed experimental trends in section 4.

II. MATERIAL AND METHODS

2.1 Materials

Studied BMC materials were compounded by Compositec (France). The polymer matrix forming these materials was prepared using a pneumatic turbine and is composed of 35.25 wt.% of orthophtalic polyester, 2.65 wt.% zinc stearate, 8.8 wt.% moulding agents and 53.30 wt.% of Al_2O_3 fillers. Final compounds were also prepared by adding to the pasty matrix glass fiber bundles made of approximately 200 fibers of length 6 mm and diameter 13.7 µm. Three mass fractions of glass fiber bundles *f* were tested, i.e. 0, 10 and 20wt.%. Here, BMC materials were collected at the outlet of an industrial injection machine.

2.2 Experimental procedure

Mechanical tests were performed using a rheometer that allows to deform samples which have characteristic dimensions that are sufficiently large compared to the lengths of fibers. It was especially developed to study the thermal-mechanical of similar polymer composites, such as Sheet Moulding Compounds, [3]. It was mounted on a MTS mechanical universal tensile testing machine having a maximum capacity of 20kN. Cylindrical BMC samples having an initial height h of 25 mm and initial diameters $2R$ of 110 mm were first processed.

III. RESULTS AND DISCUSS

3.1 General aspect of compression curves

Figure 1 represents typical evolutions of the mean axial stress $\bar{\sigma}_{33}$ with respect to the axial logarithmic strain ε_{33}. Reported curves have been obtained with five tests performed using the same testing conditions, i.e., a constant axial strain rate $D_{33} = 10^{-1}s^{-1}$, $f = 20\%$. Whatever the considered curve, three stages can be observed during these compression: in a first step, stress levels increase sharply up to first inflexion, from which they increase steadily and finally rise sharply when a second inflexion is attained for large strains.

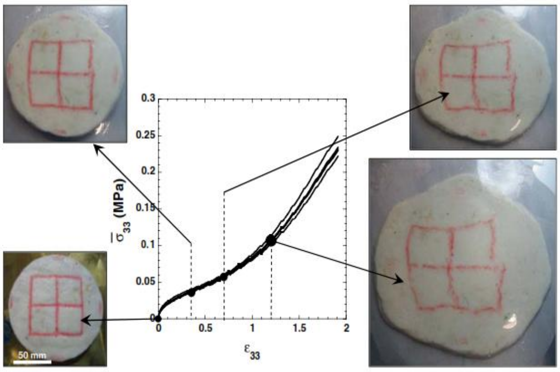

Fig.1. General aspect of a sample at different strains and typical stress-strain curves recorded for five different samples ($f = 20\%$, $D_{33} = 10^{-1}s^{-1}$).

It is worth to notice that for axial strains ε_{33} below 1.2, the scattering of the measurement is rather weak and remain below ±10%. Also notice that each stress-strain curve that will be plotted in the following will present an average curve obtained from five runs performed with the same testing conditions, as in the examples shown in Fig.1.

3.2 Influence of the strain rate

Figure 2a contains a set of representative results showing the evolution of the axial stress σ_{33} with respect to the axial strain ε_{33} for three different constant axial strain rates D_{33} and for $f = 10\%$. It clearly appears that the axial stress σ_{33} increases with both the axial strain ε_{33} and the axial strain rate D_{33}. The figure proves that BMCs exhibit strain hardening and pronounced viscous behaviour.

To better illustrate that, the evolution of the axial stress σ_{33} with the axial strain rate D_{33} for a given axial strain ε_{33} chosen equal to 0.7 is reported in Fig. 2b for all tested fiber fractions. Symbols represent the experimental points, whereas the lines represent power-laws used to fit experimental data:

$$\sigma_{33} = \mu_s(\varepsilon_{33}, f) D_{33}^{n(\varepsilon_{33}, f)} \qquad (1)$$

Where μ_s is the consistency and n the strain rate sensitivity. Both parameters are functions of the imposed axial strain ε_{33} and the fiber fraction *f*.

It notices that the shear thinning behaviour of BMC materials as $0.2 < n < 0.6$ is pronounced.

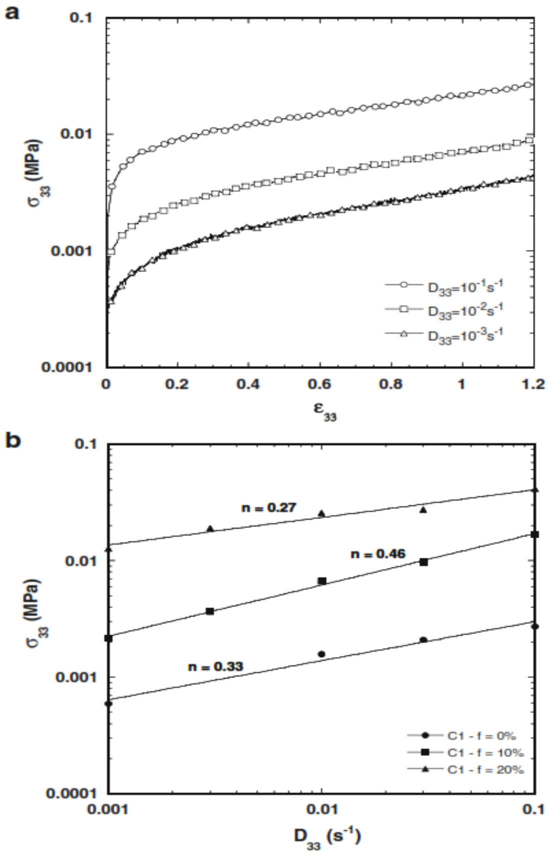

Fig.2. a. Stress-strain curves showing the influence of the axial strain rate D_{33} on the axial stress σ_{33}. b. Evolution of σ_{33} at a given axial strain ε_{33} =0.7 as a function of D_{33}, for different contents of fibers. Straight lines represent power laws used to fit the experimental data (marks).

3.3 Influence of the mass fraction

Fig.3 collects three stress–strain curves obtained when the deforming is at $D_{33} = 10^{-1}\text{s}^{-1}$. BMC samples having three different fiber mass fractions. A tremendous increase of stress levels is recorded with the fiber content. For instance, at a strain $\varepsilon_{33} = 1.2$, the axial stress measured for BMCs with *f* = 20% is 35 times higher than that of BMCs without fibers. This can be correlated to the observed increases of the consistency previously described in Fig. 2b. Please note that similar tendencies were previously observed for quite similar materials, such as SMC, [3].

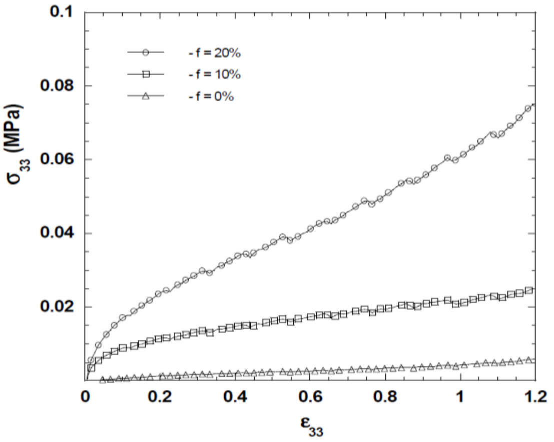

Fig. 3. Influence of the fiber content on stress-strain curves with $D_{33} = 10^{-1}s^{-1}$.

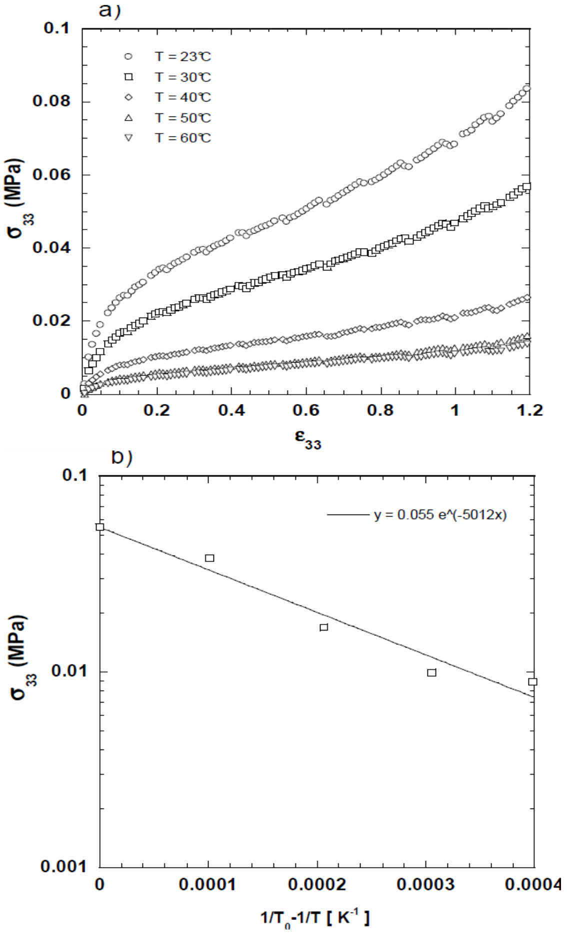

Fig. 4. Evolution of axial stress as a function of axial strain for different temperatures (a) and as a function of the temperature (b), (f = 20%, $D_{33} = 10^{-1}s^{-1}$).

3.4 Influence of the temperature

To study the influence of the temperature on stress-strain curves, we have performed compressive tests with the different temperature of samples, T = 23^{0}C, 30^{0}C, 40^{0}C, 50^{0}C and 60^{0}C.

Figure 4a shows the evolution of the axial stress as a function of axial strain for different temperatures. These results show that increasing the temperature decreases very significantly stress levels achieved during testing.

Figure 4b shows the evolution of axial stress depending on the test temperature at a strain ε_{33}=0.7. These results show that the axial stress σ_{33} obeys an Arrhenius type law:

$$\sigma_{33}(T) = \sigma_{33}(T_0)exp\left\{-b\left(\tfrac{1}{T}-\tfrac{1}{T_0}\right)\right\} \qquad (2)$$

Where b = 5012K and $\sigma_{33}(T_0)$ =0.055MPa at ε_{33}=0.7 is the axial compressive stress at the reference temperature T_0 =296K.

IV. A MACROSCOPIC VISCOELASTIC MODEL

From these experimental observations, a very simple 1D and non-linear macroscopic viscoelastic model is proposed to reproduce phenomenologically experimental trends. It is clear that more sophisticated rheological models that would account for the evolution of particles' distribution and orientation by using well chosen internal variables would be much more appropriate. However, to build them and identify their constitutive parameters, further dedicated experiments and a deeper analysis of the evolving microstructures of the suspensions would be required. The preliminary experiments presented here are not sufficient to reach this goal. Thus, the total strain rate D_{33} (resp. the strain ε_{33}) is split into two contributions, i.e. an elastic one D^e_{33} (resp. ε^e_{33}) and a purely viscous one D^v_{33} (resp. ε^v_{33}):

$$D_{33} = D^e_{33} + D^v_{33}, \qquad \varepsilon_{33} = \varepsilon^e_{33} + \varepsilon^v_{33}, \qquad (3)$$

The viscous strain rate D^v_{33} is linked with the total axial stress σ_{33} by the following constitutive equation:

$$\sigma_{33} = \eta_p(1+\alpha f^2)(D^v_{33})^n e^{k\varepsilon^v_{33}}, \qquad (4)$$

In the above equation, η_p is closely linked with the consistency of the paste without fiber at low strains. The observed strain hardening is accounted by the exponential function involving the coefficient k. Based on the results obtained with rather close polymer composites, [3] a quadratic evolution of stress levels is assumed, involving the coefficient α. The elastic strain ε^e_{33} is linked with σ_{33} by the following relation:

$$\sigma_{33} = E_p(1+\beta f)\varepsilon^e_{33}, \qquad (5)$$

Where E_p is the elastic modulus of the paste without fiber and β is a constant. Hence, the incremental form of the model reads:

$$D_{33} = \frac{\dot{\sigma}_{33}}{E_p(1+\beta f)} + \left(\frac{\sigma_{33}}{\eta_p(1+\alpha f^2)e^{k\varepsilon^V_{33}}}\right)^{\frac{1}{n}}, \qquad (6)$$

Constitutive parameters $\eta_p, \alpha, n, k, E_p, and\ \beta$, involved in the above equations, have been fitted on experimental results. They are respectively, equal to 0.004MPas, 400, 0.4, 1, 0.01 MPa and 100.

As shown in fig 6, the model permits a rather good description of experimental trends.

Based on these results, the viscoelastic model above was modified to take into account the influence of temperature as following form:

$$D_{33} = \frac{\dot{\sigma}_{33}}{E_p(1+\beta f)exp\left[-b'\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]} +$$

$$+\left(\frac{\sigma_{33}}{\eta_{BMC}(1+\alpha f^2)exp(k\varepsilon^V_{33})exp\left[-b'\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]}\right)^{\frac{1}{n}}, \qquad (7)$$

Or in simplified form:

$$D_{33} = \frac{\dot{\sigma}_{33}}{E_p(T,f)} + \left(\frac{\sigma_{33}}{\eta_{BMC}(T,f)exp(k\varepsilon^V_{33})}\right)^{\frac{1}{n}}, \qquad (8)$$

Fig.7 gives a time integration algorithm for viscoelastic model proposed.

In the same way, constitutive parameters obtained in the equations (7), have been fitted on experimental results in table below with f =20%. It notices that the parameters, *b, b'* are respectively equal to 5012K, 6536K.

***T*(K)**	***E*(MPa)**	***k***	**η_{BMC}(MPa s)**
23	0.41	1.2	0.068
30	0.25	1.25	0.046
40	0.12	1.3	0.027
50	0.064	1.35	0.016
60	0.035	1.4	0.01

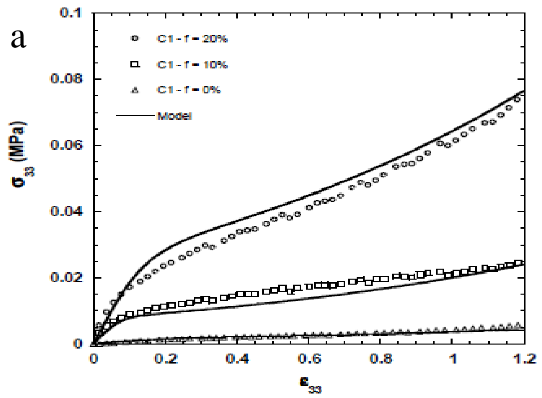

Fig. 6. Comparison between model prediction and experimental results at various fiber content (a) and at various constant (b), (f = 10%, $D_{33} = 10^{-1}s^{-1}$).

Inp s : $f, \Delta t, T, \eta_p, E_p, b, b', k, \alpha, \beta, n$

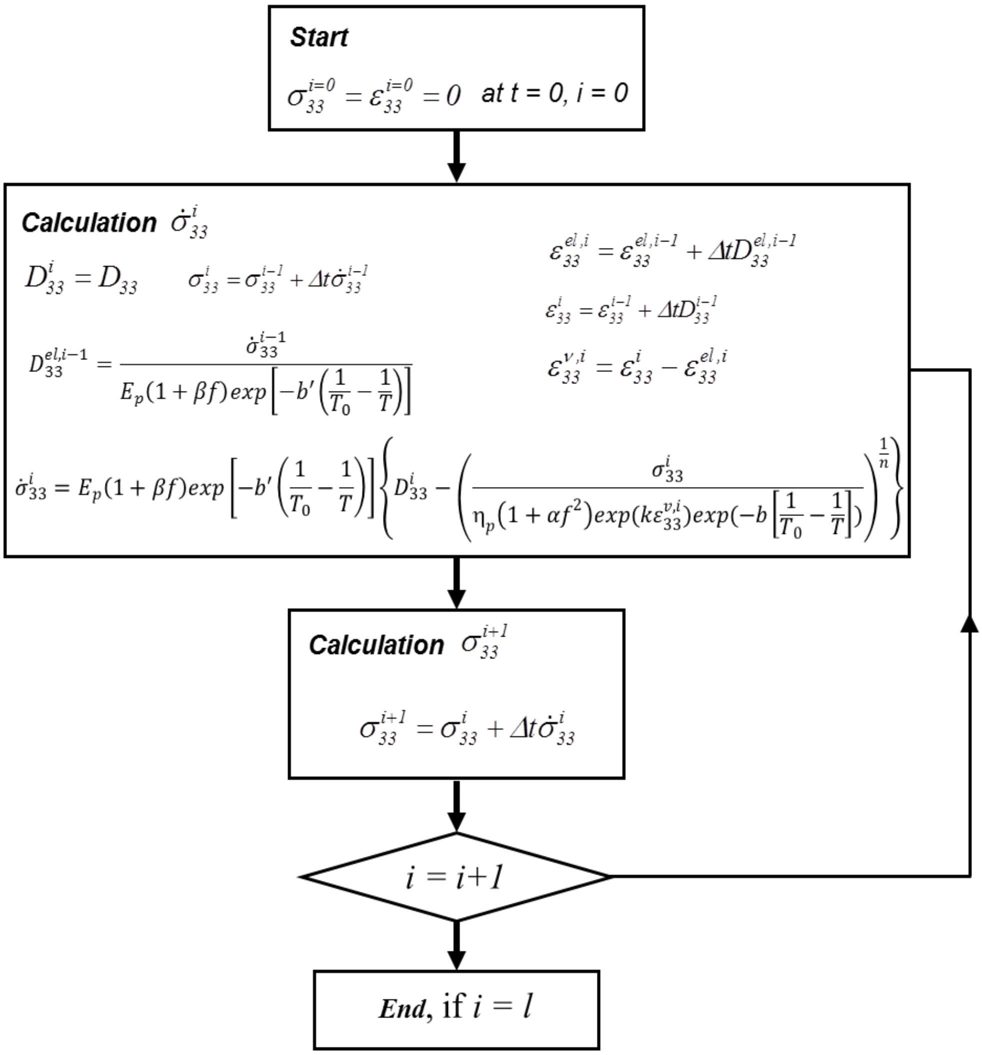

Fig. 7. Integration algorithm of nonlinear viscoelastic model.

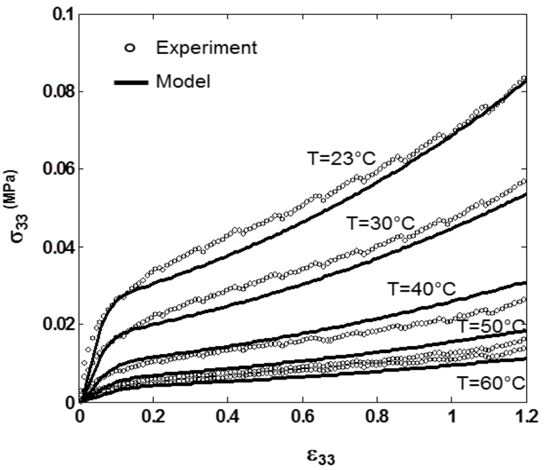

Fig. 8. Comparison between model predictionand experimental results at various temperatures.

Finally, Fig.8 compares the model predictions with experimental observations and shows a fairly good match between these two data.

V. CONCLUSION

The thermal-mechanical behaviour of BMC was here studied by performing a preliminary set of lubricated compression experiments. The experimental results emphasized the influence of the imposed strain rate, the mass fraction of fibers, as well as the temperature on the BMC behaviour

From the experimental results obtained, a model of behaviour for the BMC was proposed that allows to suitably describing the tests which have been performed on the BMC.

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