RHEOLOGICAL AND MORPHOLOGICAL INFLUENCES ON THE VISCOELASTIC BEHAVIOUR OF POLYMER COMPOSITES

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SUMMARY: This paper deals with the prediction of the shear dynamic modulus of particle or fibre-reinforced polymer composites. The Christensen-Lo self-consistent model and its (n+1)-phase Hervé-Zaoui extension are used in conjunction with the Hashin correspondence principle to perform the homogeneization from the constituent behaviours. Attention is focused on the rheological effect of an interphase and on the morphological effect of a non-uniform dispersion of the reinforcing phase. Model particle-reinforced materials have been first elaborated with controlled surface treatments and/or coating. Morphological observations are then used to build pertinent self-consistent models in each case. The method was successfully applied to the case of a unidirectional glass fibre composite.

KEYWORDS: effective properties, viscoelasticity, morphology, interphase, particle-reinforced composites, fibre-reinforced composites, epoxy, modelling.

INTRODUCTION

Homogenization techniques are currently used to predict the dynamic mechanical properties of polymer matrix reinforced by randomly dispersed particles or fibres [1-2]. The effective moduli of the composites are then calculated from the properties and the volume fractions of their constituents. However, significant discrepancies may sometimes occur between predicted and experimental behaviours of such materials. These deviations may be especially noticed when one surveys a wide range of temperature including the transition between glassy and rubber-like domains. Indeed, this transition is accompanied by an important change of the modulus contrast between the phases.

This paper deals with the shear dynamic modulus of glass-epoxy composites. The reinforcement is made of either particles or of fibres. The particle-reinforced composites are elaborated in our laboratory in order to control as much as possible the volume fraction, the surface treatment, the coating thickness and the dispersion of the beads. On the contrary, the fibre-reinforced composites are supplied by industry.

N-phase self-consistent models [3-4] allowing for calculation of the shear elastic modulus of randomly particle-reinforced composites are used. In some case, according to literature

suggestions [5], a stepwise homogeneization procedure can be performed as an alternative to the use of more complicated pattern-based models. Such an approach has been discussed in the context of polymer composites, with a particular attention to the effects of interphase, modulus contrast and connectivity [8], *i.e.* to the adequate step succession according to the heterogeneity scales in the material. Its ability to take account for special compositions and morphologies is firstly discussed in connection with the controlled materials. The conclusions prove to also hold in the case of the unidirectional composites.

EXPERIMENTAL

Materials

The composites with particles was obtained by the polymerization of an epoxy prepolymer diglycidyl ether of bisphenol A (DGEBA) provided by Dow Chemical (ref. DER 332) and the amine hardener iso-phorone-diamine (IPD) from Huls Chemical. The reinforcement was made of A-glass beads of 40µm mean diameter from Sovitec (ref. A05040). The surface of the beads was a) without any surface treatment, b) with an aminosilane sizing and c) with an elastomer coating CTBN from BF-Goodrich of 300nm thickness. Composite plates with particle volume fractions equal to 10%, 20%, 30% and 50% were molded using the following cure schedule: 1 h at 140°C followed by 6 h at 190°C. The glass transition temperature (Tg) of the epoxy resin DGEBA-IPD was 160°C as measured by DSC. Its shear moduli were 2500MPa in the glassy state and 18MPa in the rubbery plateau. For the elastomer CTBN, Tg was -33°C, and moduli 930MPa and 4.5MPa respectively.

In the case of the unidirectional composites, the DGEBA epoxy prepolymer was cured with the hardener dicyandiamide (DDA). E-glass fibres were provided by Vetrotex-St. Gobain with commercial sizing (ref. P185 from Vetrotex). Two different fibre diameters were used: 13 and 20µm. Composite plates were supplied by Renault and Brochier. They were molded from composite prepregs using the cure schedule: 6mn at 155°C followed by 2h at 140°C. The volume fractions of glass in the composites were determined by pyrolysis at 625°C to constant weight: they ranged from 43% to 68%. Tg of DGEBA-DDA was now 139°C and the glassy and rubbery shear moduli were 1840MPa and 15.3MPa respectively.

Morphological observations were carried out by optical microscopy (Zeiss) on all the composites. In the case of particle-reinforcement, they showed a uniform dispersion of the beads in the matrix for the lower concentrations (≤20%) whatever the material. On the contrary, aggregates, the more important as the higher concentration, take place in the case of untreated beads. This phenomenon appears less perceptibly when the beads are sized or coated, may be due to a dispersing effect of the treatment in the blend before curing. In the unidirectional composite, aggregates are always present whatever the fibre concentration. This is probably due to the initial wisp disposition of the fibres and to the difficulty to erase the initial form of the prepregs during process.

Experimental technique

Dynamic mechanical measurements were performed with a forced-oscillation pendulum working in torsion and involving small stress amplitude insuring a linear response of strain with respect to stress. In order to detect relaxation processes in the polymer, the measurements were done at the frequency of 1Hz in a wide range of temperature from 100K to 450K, including the glass transition. The data (elastic shear modulus G', dissipative one G" and loss factor tanϕ) were plotted versus temperature.

MICROMECHANICAL ANALYSIS

When a single uniform reinforcing phase is included in a uniform matrix, the 3-phase Christensen-Lo (C-L) self-consistent model [3] is well suited for homogeneization of elastic randomly reinforced composites. It can be easily enlarged to linear viscoelasticity, assuming the Hashin correspondence principle [6] that substitutes complex moduli to the elastic ones. The (n+1) phase Hervé-Zaoui (H-Z) model [4] extends the C-L model to account for either true multi-layered inclusions or for property gradients at the inclusion-matrix interfaces. Thanks to the randomly spatial phase disposition, the morphology is only described by the volume fractions of the constituents anyway. Some difficulties arise with more complicated morphologies, especially when reinforcement is no longer randomly dispersed. One route can be followed where the morphology is statistically described before calculating the material property [7]. Such approaches lead to complex theoretical models and involve very sophisticated tools to characterize the morphology.

As an alternative route, Christensen [5] has suggested to estimate the effective properties of materials exhibiting several scales of heterogeneity by the n-step repetition of the 3-phase C-L model. As it has been shown in the previous section, most of our composites contain aggregates. In the presence of such clusters, two or more scales of heterogeneity can be distinguished. The aggregates are a first composite at the lower scale whereas the real material is a composite of composite phases at the macroscopic scale.

Repeated n-phase model

In order to emphasise on the manner to account for each effect, we will use here more and more sophisticated models according with the increasing complexity of the material morphology. The considered morphologies are schematically presented on Fig. 1 irrespective to the real scales and the corresponding calculations are presented below.

When the reinforcements are randomly dispersed in the matrix, the self-consistent model is applied only once. For the case shown on Fig. 1-a, the 3 phases are outwardly: reinforcement in matrix in equivalent homogeneous medium (model A). For coated fillers as on Fig. 1-b, the 4 phases are reinforcement in interphase in matrix in e.h.m (model B).

The figure 1-c shows a two-scale morphology that exhibits non-reinforced zones and highly reinforced ones (model C). The latter can be considered itself as a concentrated composite with a volume fraction of reinforcement V_c greater than the nominal one V_n in the real composite. The 3-phase model should be applied firstly, as in the case of Fig. 1-a, to obtain the effective moduli of this concentrated composite and one more time, in the same manner, to obtain those of the real composite by considering the non-reinforced zone of volume fraction $V_u=1-V_n/V_c$ included in the concentrated composite in the real e.h.m.

Finally, the figure 1-d depicts a peculiar morphology in which very close reinforcements are connected by a thin interphase (model D). Different authors [9-10] suggested that the layer of polymer that is in contact with a hard reinforcement might have a very lower mobility than the rest of the matrix. So, the connecting interphase becomes a binder of the reinforcements and a trap for the interstitial resin. Then, thanks to the connectivity, we tried to describe such morphology by means of the inwardly 3-step repetition of the 3-phase model as schematically shown on Fig. 2.

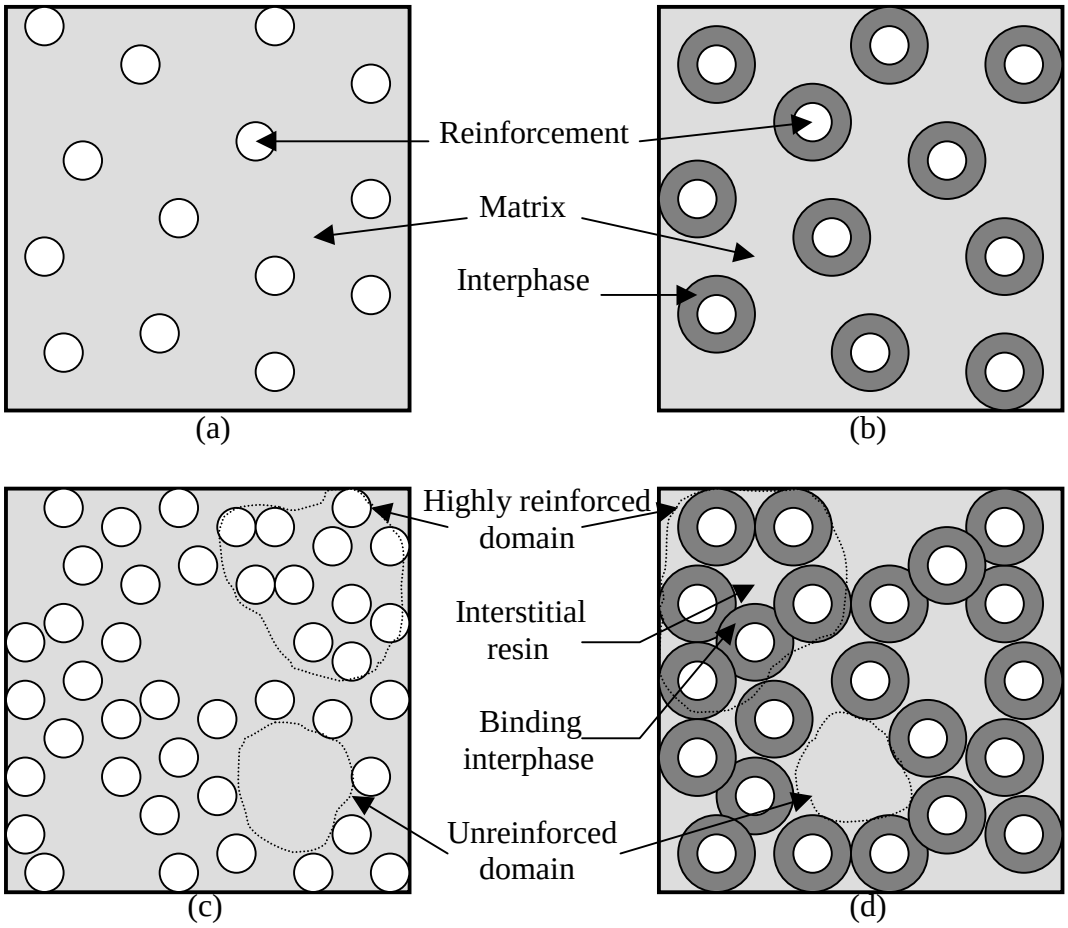


Fig. 1: Schematic description of morphologies

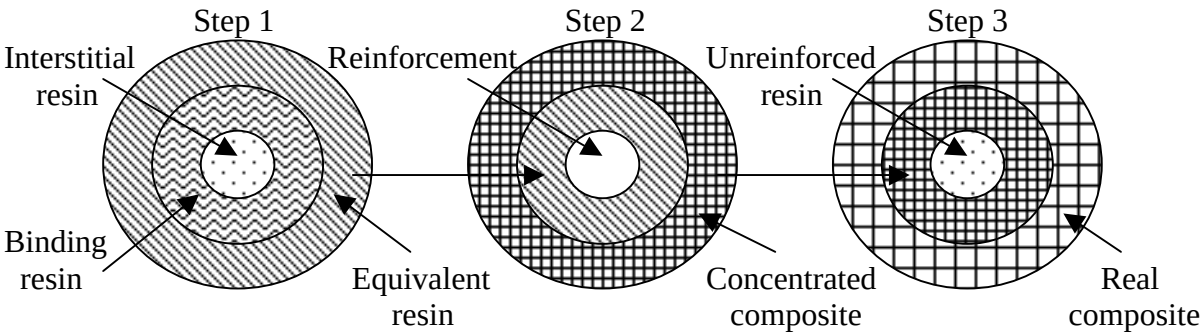


Fig. 2: Schematic framework of the inwardly 3-step repetition of the 3-phase model

The first step gives the effective moduli of an equivalent resin *i.e.* both the binding resin and the interstitial resin included in the concentrated composite. The binding resin behaves then as a shell trapping the interstitial one [8,14]. After that, this equivalent resin is considered as the matrix surrounding the reinforcements in order to obtain the properties of the concentrated composite when the second step is achieved. Lastly, in the third step, this concentrated composite becomes the matrix of a composite that the non-reinforced zones are the inclusions.

APPLICATIONS

The viscoelastic properties of the resins DGEBA-IPD and DGEBA-DDA were measured. The shear elastic modulus G' and the loss factor tan(ϕ) of DGEBA-IPD are plotted versus temperature in Fig. 3. The loss factor shows two peaks at 239K and 446K referred to as β and α-processes respectively. The drop in modulus corresponding to the main α-relaxation is associated to the glass transition. The viscoelastic properties of the elastomer CTBN were found in Ref. 11. As reported by Agbossou [12], the Poisson's ratio of the polymer materials was continuously increased from 0.32 to 0.5 during the glass transition. The glass was assumed to be elastic linear and its shear modulus is equal to 30GPa all over the temperature range.

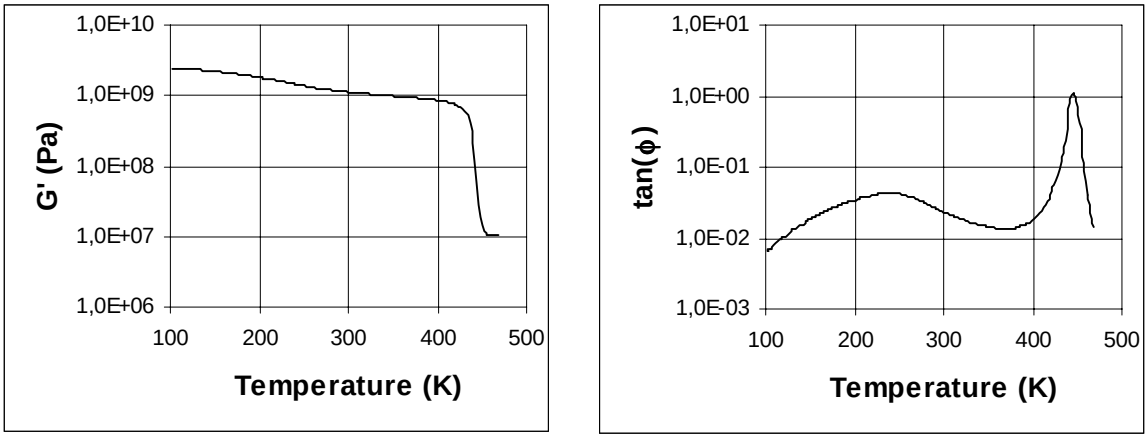


Fig. 3: Shear elastic modulus and loss factor of the epoxy resin DGEBA-IPD

The material properties of all the constituents being known, the effective complex shear modulus was calculated at any temperature and it was compared to the experimental results measured on the composite materials.

Model particle-reinforced composites

In a first time, we considered composites with untreated beads. The results obtained by application of the model A were in good agreement with experimental ones in the case of the lower volume fractions of filler that are then almost randomly dispersed. On the other hand, the figure 4 shows the comparison of the elastic shear modulus of the 30%-v.f. composite calculated from the model A with the experimental results. This model that does not account for clusters under-estimate clearly the modulus above the main relaxation temperature. This discrepancy disappears, as shown on Fig. 5-a, with the model C if the volume fraction V_c in the highly reinforced zones is adjusted to 51%. This high value is in accordance with the morphology observed by microscopy. The figure 5-b shows the loss factor that is very correctly estimated too. The application of the model C to the 50%-v.f. composite leads to an adjusted value of V_c of 65%. The results are shown on Fig. 6.

The same comparison with the model C is now presented on Fig. 7 in the case of the 30%-v.f. composite filled by beads treated with the aminosilane sizing. The adjusted volume fraction V_c is now of 38% only, according with the better dispersion of the treated beads than of the untreated ones.

So, these observations point out the morphological effect of the non-uniform dispersion of the filler in the composite. The more important are the aggregates, the more the mechanical behaviour of the composites deviates from that of randomly reinforced ones.

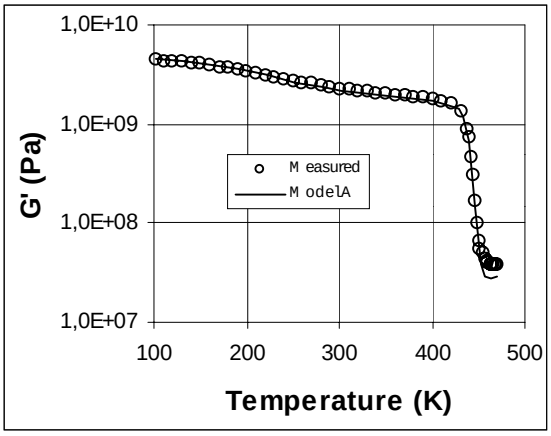
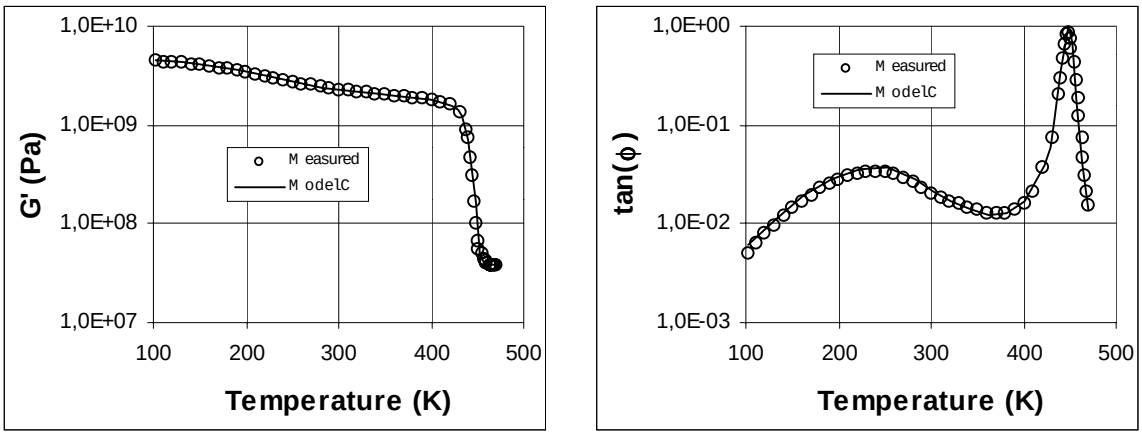


Fig. 4: Shear elastic modulus of the 30% v.f. untreated bead composite
Comparison model A with measurements



(a) (b)

Fig. 5: Shear elastic modulus (a) and loss factor (b) of the 30% v.f. untreated bead composite
Comparison model C (V_c=51%) with measurements

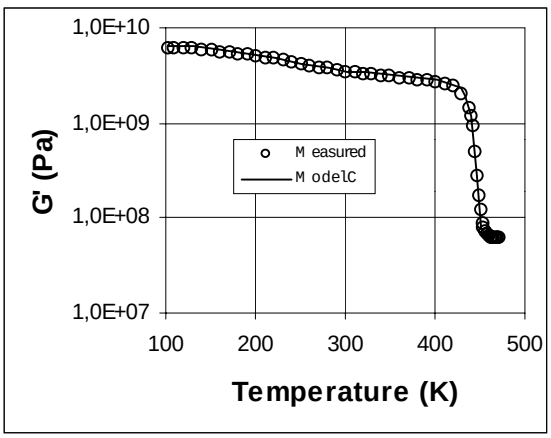


Fig. 6: Shear elastic modulus of the 50% v.f. untreated bead composite

Comparison model C (V_c=65%) with measurements

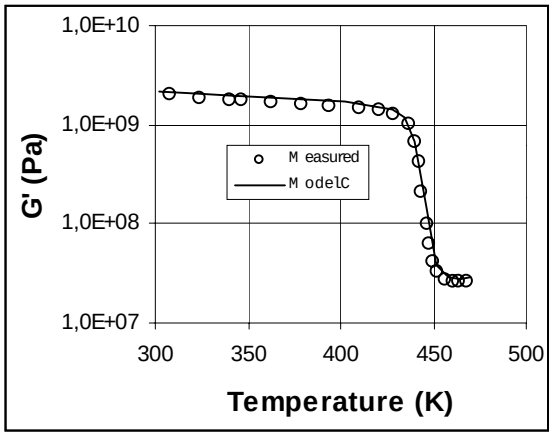
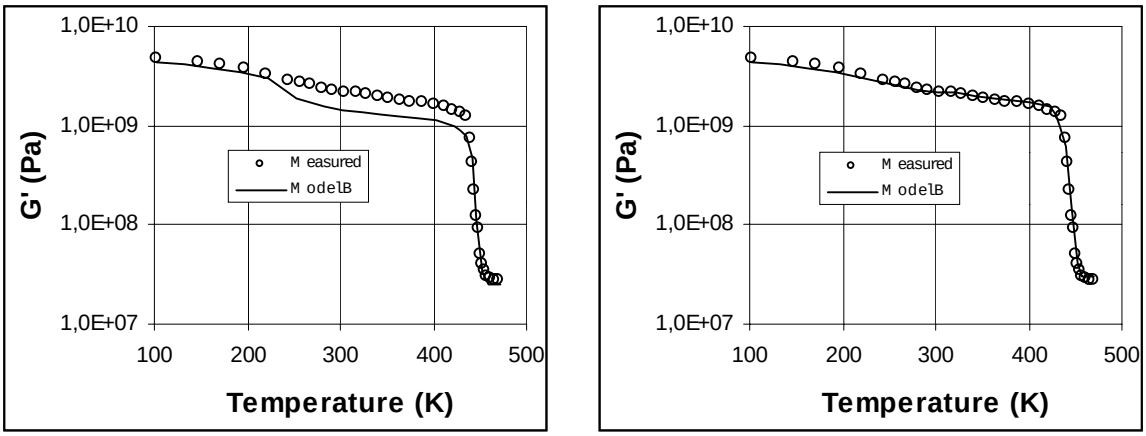


Fig. 7: Shear elastic modulus of the 30% v.f. sized bead composite
Comparison model C (V_c=38%) with measurements

The effective shear modulus of composites filled by elastomer coated beads was determined from the model B. The figure 8-a shows a deviation above the temperature Tg of the elastomer near 240K. Following Marques [13] who suggested an increase of the α-relaxation temperature in a thin interphase, the properties of the elastomer were modified so that its glassy plateau was pursued above Tg and its loss factor was kept constant. Then, the previous discrepancy disappears as shown on Fig. 8-b. Now, these observations point out clearly a rheological effect of the glass-elastomer interface.



(a) (b)

Fig. 8: Shear elastic modulus of the 30% v.f. coated bead composite
a) natural interphase CTBN – b) modified interphase

Fibre-reinforced composites

The same procedure has also been applied to commercial unidirectional composites with the aim of predicting the dynamic longitudinal shear modulus. Morphological and rheological aspects of the effective modulus prediction are now emphasised for a 52% v.f. fibre-reinforced composite [14]. The figure 9-a shows the results obtained for the elastic shear modulus from the model A. This modulus is under-estimated on the full temperature range. The deviation is mainly due to a poor description of the morphology that indeed presents wide zones without fibres.

The results are then improved by proceeding to a 2-step homogeneization with the model C. According to estimation from a micrography of a right section of the composite, the volume fraction V_c in the concentrated zone is 74%. As see on Fig. 9-b, the elastic shear modulus is now well estimated below the α-relaxation temperature, but it remains too weak above Tg. This last disagreement is finally rectified by accounting for the binding effect of a 50nm-thickness layer of modified resin. As in the case of the above bead coating, the properties of the epoxy resin in the interphase were modified so that its glassy plateau was pursued above Tg and its loss factor was kept constant. The results shown on Fig. 9-c are then in very good agreement all over the temperature range.

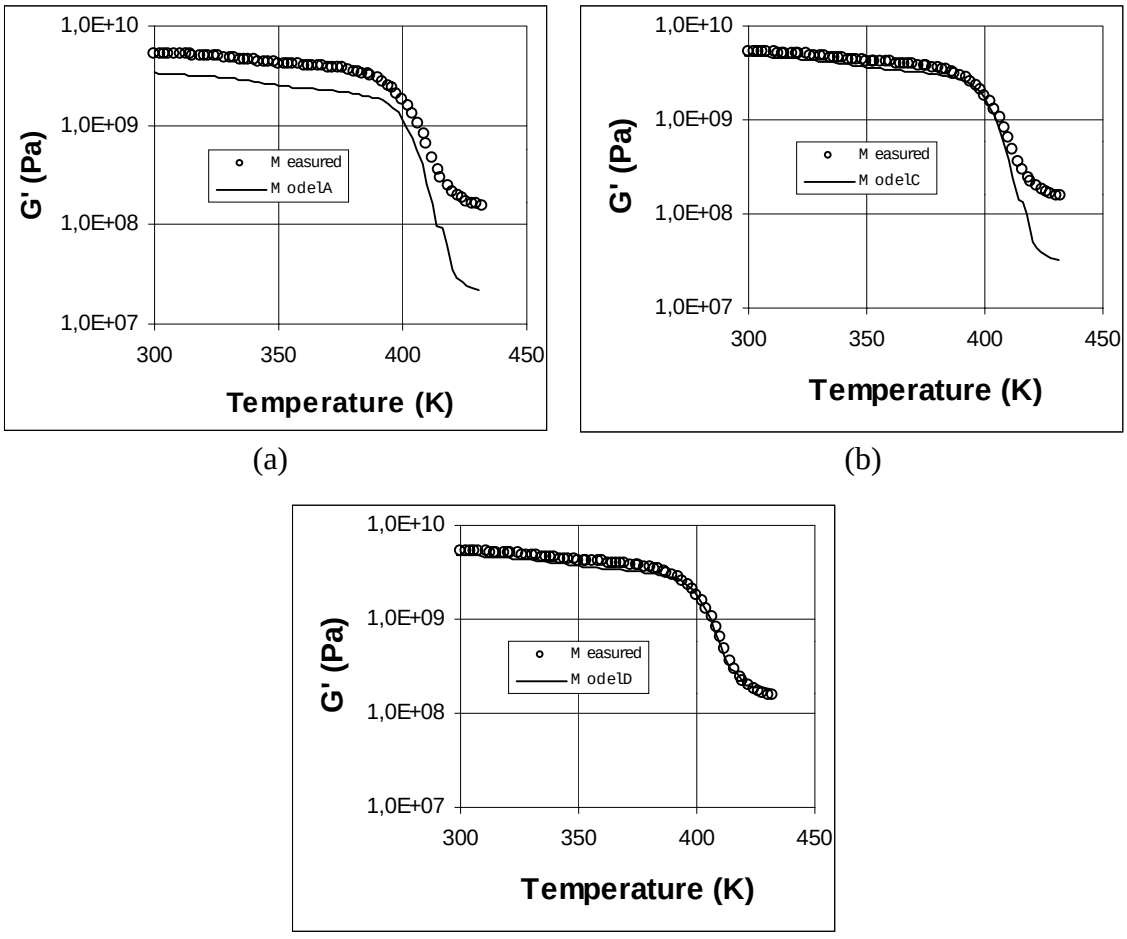


Fig. 9: Longitudinal shear elastic modulus of the 52% v.f. fibre-reinforced composite. Estimations from a) the 1-step model, b) the 2-step model and c) the 3-step model

CONCLUSIONS

Dynamic mechanical analysis is a well-suited technique to study the linear viscoelastic properties of heterogeneous materials. Indeed, it allows for looking for the individual relaxation processes of the composite constituents. This technique was applied on model materials with controlled morphologies and controlled interphases. An interface effect on the material behaviour was evidenced: the molecular mobility of a thin interphase is reduced above Tg.

Several models were developed to predict the effective dynamic shear modulus of composites from the behaviour of their constituents. These models are grounded on self-consistent schemes allowing for randomly reinforced composites. Morphological effects as non-uniform dispersion of the reinforcements are considered thanks to the presence of more than one heterogeneity scale. Then multi-step analyses were successfully processed. The individual influences of each morphological or rheological particularity were pointed out by means of a progressive increase of complexity. Each modelling concept was firstly validated with experimental comparisons performed on adequate model materials. The conclusions are also valid for commercial fibre-reinforced materials. The binder effect in clusters of a modified interphase is well established.

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