Dynamic Mechanical Analysis of Multiphase Polymeric Composite Materials

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The paper aims to present a theoretical-experimental approach of a particular class of composite materials known as multiphase composites in order to retrieve its effective dynamic moduli and identify the major influencing factors on these variations. Supplementary, will be presented a two step homogenization concept based on the well known theoretical predictions from the micromechanics of composite materials approaches, the Mori-Tanaka that applies to the particle reinforced composites and Halpin-Tsai that applies to the random fibre composites. The theoretical values were compared with the experimental data, the later being retrieved during a two heating cycles with temperature ranging from -30^{0}C to 160^0/200^{0}C, in air, at a frequency of 1 Hz, using a DMA 242 C device, from Netzsch, Germany. The samples were manufactured using a self-developed technology. The samples were ceramics (Al_2O_3) and metal (Fe) reinforced particles embedded in small volume fraction along with random E-glass fibres (65%) into a polymeric matrix material.

Keywords: composites, multiphase, polymer, dynamic modulus, testing

Understanding polymeric composites behaviour under a dynamic regime is not an easy task to accomplish or predict. Technical literature lack of intensive studies on this area is mainly due to the high acquisition cost of the research equipment or restrictive accessibility to a data base on polymers properties. Nevertheless, there are several authors that were approaching this type of experimental investigation on the class of composite materials, in their classic formulae – one constitutive embedded into a matrix, in pursue of retrieving the dynamic elastic modulus, the most comprehensive material property [1-2,5, 6].

Multiphase polymeric composite materials represents a new class of materials that allow various combinations among its constitutive – fibre & fibre, particle & fibre, particle & particle, in different volume fraction, from different materials (materials compatibility has to be assured previously), all of them allowing mechanical, electrical, or thermal properties tailoring depending on the application [7, 8, 10].

It is natural that, in such circumstances, a new methodology has to emerge to allow the characterization of this class of materials, a new approach like the one developed by the authors of this paper, theoretically and experimentally. From theoretical point of view, the idea behind is a simple one and involves a two step homogenization process based on two well known theoretical models such as Mori-Tanaka theoretical model – a generalized self-consistent scheme for particle reinforced composite materials effective elastic properties prediction, independently on the particles size distribution and the Halpin-Tsai model, respectively.

Supplementary, the theoretical approach is accompanied by experimental research such as dynamic mechanical measurements carried out on multiphase composite structures samples. The samples were manufactured on a self-developed technology bases, the phases consisting of ceramics and metal particles embedded along with long, random E-glass fibres into a polymeric matrix. The data, either from theoretical prediction or experimentally retrieved were not compared with similar data from technical literature due to the lack of the latter and restricted access in case of availability [9].

Theoretical approach

In order to be able to predict, closer to reality, the effective dynamic moduli of the multiphase composite materials such are those approached herein, a two step homogenization procedure was proposed. Consequently, in the first step were subjected to the homogenization process the particles, in their dilute concentration, and the matrix leading to the so called homogeneous equivalent matrix. The effective dynamic elastic properties of the combinations were predicted using the Mori-Tanaka theoretical model that applies to the small volume fraction of particles embedded into a matrix material. In this case the complex compressibility and complex shear elastic moduli can be predicted from the following expressions [3,4]:

$$K^*_{em} = K^*_m + \frac{V_p \cdot K^*_m \cdot \left(K^*_p - K^*_m\right)}{K^*_m + \xi \cdot \left(1 - V_p\right) \cdot \left(K^*_p - K^*_m\right)}, \tag{1}$$

$$G^*_{em} = G^*_m + \frac{V_p \cdot G^*_m \cdot \left(G^*_p - G^*_m\right)}{K^*_m + \varsigma \cdot \left(1 - V_p\right) \cdot \left(G^*_p - G^*_m\right)}. \tag{2}$$

where ζ and ς are expressed as:

$$\xi = \frac{1 + \nu_m}{3 \cdot \left(1 - \nu_m\right)}, \tag{3}$$

$$\varsigma = \frac{2 \cdot \left(4 - 5\nu_m\right)}{15 \cdot \left(1 - \nu_m\right)}. \tag{4}$$

The complex elastic moduli of the equivalent matrix can be expressed taking into account the previous expressions of the bulk and shear moduli by the aid of the well known relationship:

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$$E_{em}^{*} = \frac{9 \cdot K_{em}^{*} \cdot G_{em}^{*}}{3K_{em}^{*} + G_{em}^{*}} \quad (5)$$

In the 2-nd step of the homogenization process the phases were considered to be the discontinuous fibres, randomly distributed and the equivalent matrix from previous step, leading to a homogeneous composite medium for which its effective dynamic modulus have been retrieved applying the Halpin-Tsai theoretical model.

It is well know that the elastic modulus in case of random fibres reinforced composite materials can be predicted by the aid of relation [2,3]:

$$E_{c}^{*} = \frac{3}{8} \cdot E_{1}^{*} + \frac{5}{8} \cdot E_{2}^{*}, \quad (6)$$

where E^{*}_{1} and E^{*}_{2} represents the longitudinal and transversal, respectively, complex elastic moduli for unidirectional, discontinuous fibre reinforced composite materials, moduli that can be written function of fibres diameter and length by the aid of Halpin-Tsai expressions [2,3]:

$$E_{1}^{*} = E_{em}^{*} \cdot \frac{1 + 2 \cdot \eta_{L}^{*} \cdot V_{f} \cdot \frac{l}{d}}{1 - \eta_{L}^{*} \cdot V_{f}}, \quad (7a)$$

$$E_{2}^{*} = E_{em}^{*} \cdot \frac{1 + 2 \cdot \eta_{T}^{*} \cdot V_{f}}{1 - \eta_{T}^{*} \cdot V_{f}}, \quad (7b)$$

where η_L and η_T are expressed by:

$$\eta_{L}^{*} = \frac{\frac{E_{f}^{*}}{E_{em}^{*}} - 1}{\frac{E_{f}^{*}}{E_{em}^{*}} + 2 \cdot \frac{l}{d}}, \quad (8a)$$

$$\eta_{T}^{*} = \frac{\frac{E_{f}^{*}}{E_{em}^{*}} - 1}{\frac{E_{f}^{*}}{E_{em}^{*}} + 2}. \quad (8b)$$

All these successive replacements, especially those due to the complex form of the elastic moduli, lead to a huge mathematical computation that was not covered or presented herein. As a simple matter of fact, expression (9) represents one of the simplest expressions for the loss factor corresponding to the effective multiphase polymeric composite material, after the 2nd homogenization step:
where:

$$tg\delta_{c} = \frac{E_{c}''}{E_{c}'} = \frac{3 \cdot tg\delta_{m} \cdot \left(1 + 2 \cdot \xi \cdot \eta_{L}'' \cdot V_{f}\right) \cdot \left(1 - \eta_{T}'' \cdot V_{f}\right) + 5 \cdot tg\delta_{m} \cdot \left(1 + 2 \cdot \eta_{T}'' \cdot V_{f}\right) \cdot \left(1 - \eta_{L}'' \cdot V_{f}\right)}{3 \cdot \left(1 + 2 \cdot \xi \cdot \eta_{L}' \cdot V_{f}\right) \cdot \left(1 - \eta_{T}' \cdot V_{f}\right) + 5 \cdot \left(1 + 2 \cdot \eta_{T}' \cdot V_{f}\right) \cdot \left(1 - \eta_{L}' \cdot V_{f}\right)} \cdot \frac{\left(1 - \eta_{L}' \cdot V_{f}\right) \cdot \left(1 - \eta_{T}' \cdot V_{f}\right)}{\left(1 - \eta_{L}'' \cdot V_{f}\right) \cdot \left(1 - \eta_{T}'' \cdot V_{f}\right)} \quad (9)$$

$$\eta_{L}'' = \frac{\left(\frac{E_{f}'}{E_{em}'}\right) \cdot tg\delta_{f} - tg\delta_{m}}{\left(\frac{E_{f}'}{E_{em}'}\right) \cdot tg\delta_{f} + 2 \cdot \xi \cdot tg\delta_{m}}, \quad (10a)$$

$$\eta_{T}'' = \frac{\left(\frac{E_{f}'}{E_{em}'}\right) \cdot tg\delta_{f} - tg\delta_{m}}{\left(\frac{E_{f}'}{E_{em}'}\right) \cdot tg\delta_{f} + 2 \cdot tg\delta_{m}}, \quad (10b)$$

$$\eta_{L}' = \frac{\left(\frac{E_{f}'}{E_{m}'}\right) - 1}{\left(\frac{E_{f}'}{E_{m}'}\right) + 2}, \quad (10c)$$

$$\eta_{T}' = \frac{\left(\frac{E_{f}'}{E_{m}'}\right) - 1}{\left(\frac{E_{f}'}{E_{m}'}\right) + 2 \cdot \xi}, \quad (10d)$$

In the previous expressions the general complex expression of the property (e.g. Young modulus of matrix, fibres, composite etc.) considered is given by $P^{*} = P' + i \cdot P''$, P' being the storage component and P" the dissipation component, and the loss factor by $tg\delta = P'' / P'$.

Supplementary, were used the following terms that stand for: V_f – fibre volume fraction, V_p – particle volume fraction, E – Young modulus, G – shear modulus, K – bulk modulus, ν – Poisson ratio, l - fibre length, d – fibre diameter and $\zeta = l / d$. As one can easily figure out, the indices stand for: f – fibres, p – particles, m – matrix, em –equivalent matrix, c – composite. Supplementary, each phase was considered as being isotropic and void content as being negligible.

Experimental part

Materials

Samples under experimental investigation were manufactured to form a multiphase structure made up from two different constitutive – fibres and particles - embedded in different volume fraction into a polymeric material. The composite matrix was chosen as being a polyester resin, Synolite 8388 P2, made by DSM Composite Resins (Switzerland), due to its good interfacing properties. The particle inclusions were considered: ceramic materials (with a high content of Al_2O_3), made from a natural stone, characterized as having a relatively high purity and provided by Alpha Calcite, Germany under the Alfrimal registered trade-mark and technical pure iron, respectively. Both particle types were mixed within the polyester resin mass in 5% and 10% respectively, volume fraction.

The 3rd phase chosen were E-glass type random fibres, known as MultiStratTM Mat ES 33-0-25, made by Johns Manville, SUA, being characterized as having a 65% volume fraction. The additives used were chosen as being chemical compounds showing compatibility with the other phases and allowing polymerization process initiation and development.

A reference sample made up only from fibres, with the same volume fraction as the other ones, was manufactured to aid the experimental data comparison and the tailoring process with respect to the effective elastic properties of structures.

Experimental investigation

Samples of reference and multiphase composite materials (dimensions: 50x10x5 mm) were subjected to 3 point bending under a temperature imposed program, in air, using a DMA 242 C device, from Netzsch, Germany.

The effective dynamic moduli of each class of composite materials and their temperature dependence were provided directly by the testing machine software called Proteus. The experimental investigations were done using the following settings: temperature program -30 to 160/ 200^0 C, heating rate 2 K/min, frequency 1 Hz, and maximum dynamic force of 6.1 N. The higher temperature value was chosen according to the behaviour of the matrix polymeric material. Simple experimental observation were showing a strong oxidation process taking place above the maximum value imposed herein and some practical aspects, such as long time consuming for each samples, were few reasons that help in choosing this temperature range.

Sensitivity analysis

The sensitivity analysis was carried out using the @RISK 5.5 from Palisade, U.S.A. As input parameters were chosen the volume fraction and the elastic properties of each constitutive, the latter considered as having each a normal distribution, the output being in this case the effective dynamic elastic moduli of the multiphase polymeric composite, in its modulus value. Using only 5 simulations and 5000 iterations will be enough to underline the major influencing constitutive elastic properties on the overall dynamic modulus of the multiphase composite as it can be seen from the resulting Tornado graphs.

Results and discussion

The multiphase polymeric composite materials were manufactured as having a highly dispersed phase given by the particles embedded into the polymeric matrix in different but small volume fraction. This can be seen from figure 1 which represents a SEM view of one composite structure made from Fe particles (10%) and E-glass fibres (65%) embedded into a polymeric matrix material.

Figures 2 and 3 are process curves retrieved during the dynamic mechanical tests carried out for a temperature range from -30^0C to $160^0/200^0$C, for the reference sample (no particles) and for a sample of a multiphase composite reinforced with ceramic particles and random glass fibres, respectively. The data corresponds to the temperature dependence of the storage (real component) and the loss

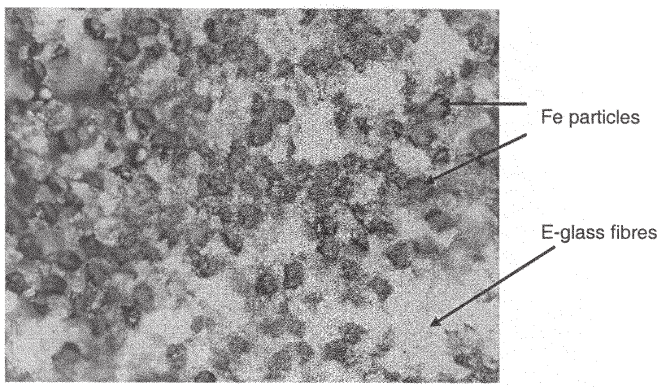

Fig. 1 SEM (x500) view of a 10% Fe, 65% E-glass fibres polymeric multiphase composite material structure

(complex component) of the dynamic elastic moduli, as well to the loss factor given as a ratio of the previous ones. The curves were superimposed and corresponds to two heating cycles for each samples investigated. The heating processes are data consuming and usually 2 processes are considered, the second offering the proper results due to the stress relaxing effects that are taking place.

In figure 2 the first heating process revealed two transitions during the measurements, an onset in the E' curve at 60^0C with corresponding value at 74^0C on the E'' curve, and at 95^0C in the storage modulus curve with the corresponding value at 97^0C on the loss modulus curve. During the second heating the first transition disappears and the second transition stays nearly constant (E' – 81^0C, E'' – 99^0C, tan d – 112^0C) which is due to the post curing of the material.

Figure 3 represents a DMA process curves for a 10% ceramic particles embedded along with 65% glass fibres into a polymeric matrix. As for the reference sample, two transitions were measured – one at 59^0C (69^0C on the E'' curve) and the other at 83^0C (85^0C on the E'' curve) in the E' curve. During the second heating the first transition disappears.

Definitely, the constitutive are influencing the overall dynamic behaviour of the multiphase composite structure.

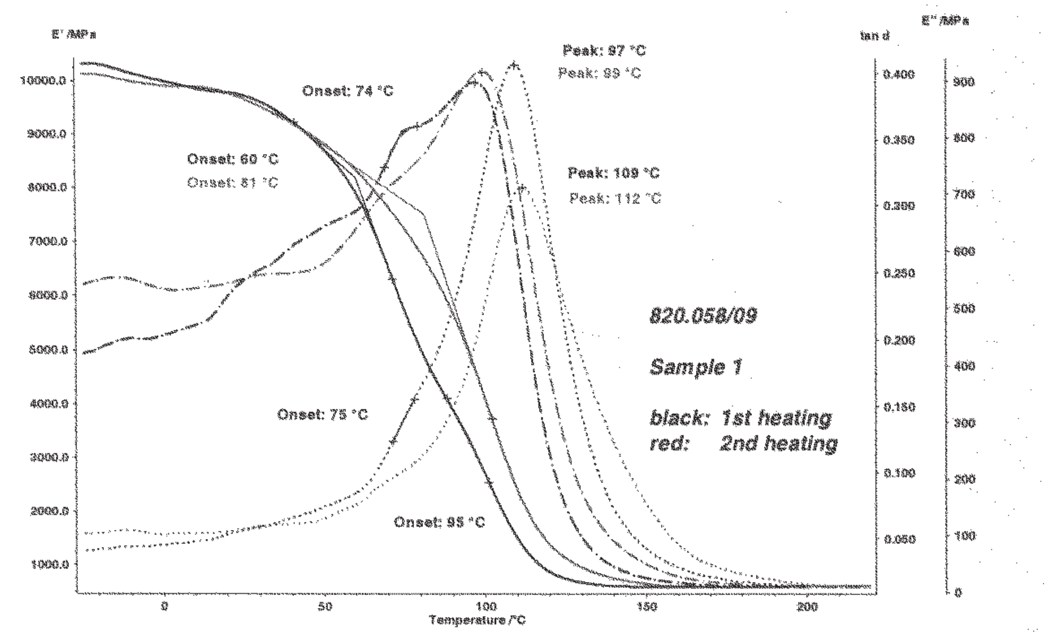

Fig. 2 Temperature dependence of the storage modulus E´, loss modulus E´´ and the loss factor tan δ of reference sample

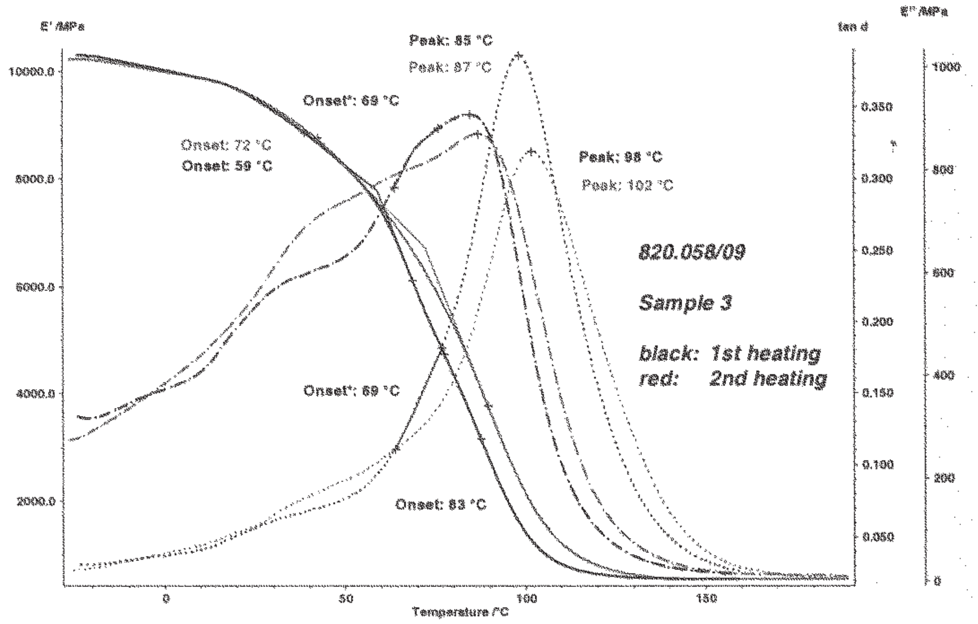

Fig. 3 Temperature dependence of the storage modulus E´, loss modulus E´´ and the loss factor tan δ of a 10% ceramic, 65% E-glass fibres multiphase composite material structure

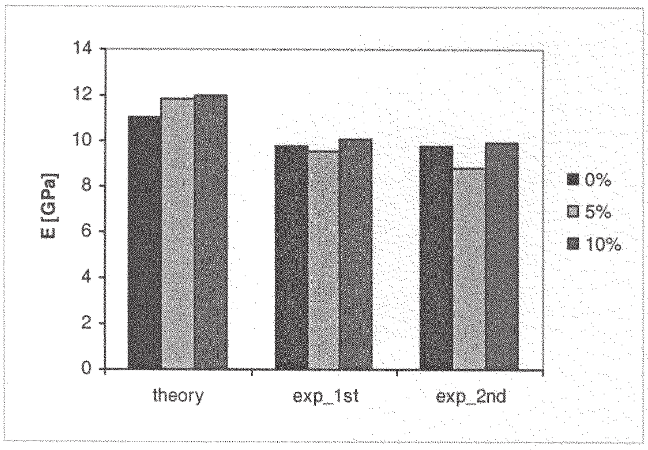

Fig. 4 Theoretical vs. experimental effective dynamic moduli for a 5% Fe, 65% E-glass fibres multiphase polymeric composite sample

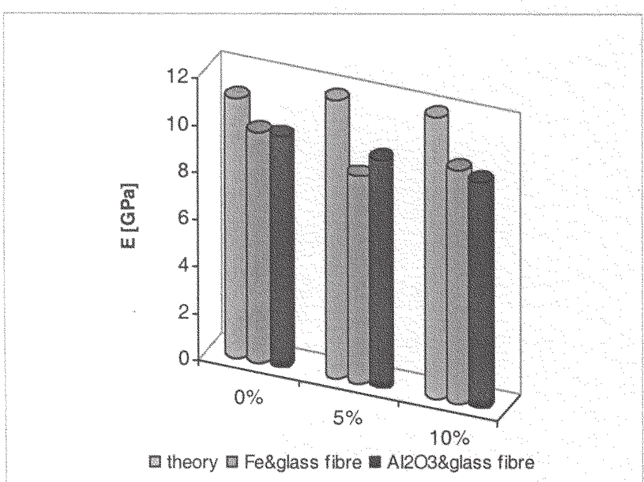

Fig. 5 Theoretical vs. experimental effective dynamic moduli for the samples made from Fe and Al2O3 particles (5% and 10%) and 65% E-glass fibres (values corresponding to a 22^0 C temperature, 2^{nd} heating process)

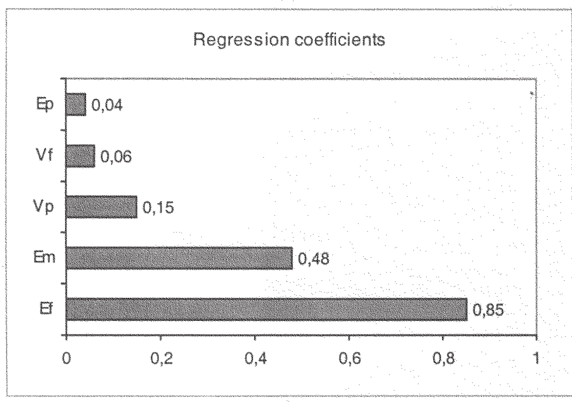

Fig. 6 Tornado graph output from the sensitivity simulations on a 10% Fe, 65% E-glass multiphase polymeric composite material (@RISK 5.5)

As it can be seen from figure 4 or figure 5, there are small differences among the experimental values corresponding to the 1^{st} or the 2^{nd} heating stage. The decrease taking place in the experimental data after a 2^{nd} heating cycles is registered in the loss modulus, meaning the fact that the polymer material is rearranging its molecular structure and the polymerization process was reaching a final stage. The particle volume fraction increase do not give rise to huge changes on the dynamic modulus, fact that is quite reasonable taking into account the small amount involved. Consequently, for the effective dynamic moduli trend are responsible mainly the random glass fibres and the polymeric matrix material.

In figure 6 are represented the results of the simulations of the sensitivity analysis done on a 10% Fe particles and 65% E-glass fibres combination for the multiphase polymeric composite in order to underline the major influencing factors on the effective dynamic modulus. From the simulated data it is obvious that the fibres and the matrix are the dominating factors on the effective dynamic moduli of the multiphase composite, meaning the fact that these types of constitutive can be subjected to changes in order to tailor the overall elastic property.

Conclusions

Multiphase polymeric composite materials represent a new emerging class of materials that can be tailored into many ways to achieve certain mechanical properties. Dynamical mechanical testing is one of the most powerful experimental configuration that allows to retrieve information on the individual constitutive and from a restricted perspective to size the structural changes inside the samples. The experimental research and theoretical approach of this class of multiphase composite materials – particle & fibres – allowed to retrieve their dynamic moduli and to identify the dominating factors upon the elastic properties.

Consequently, taking into account all the observations, it can be concluded the fact that dynamic mechanical analysis (DMA) ties together information on:

- molecular structure - phases, relaxation mechanisms, free volume, etc.;
- structure properties – adhesion, temperature performance, long term behaviour, dimensional stability, etc.;
- manufacturing conditions – temperature, stress, strain, heat history, etc.,
- contributing each, in some extent, on the effective elastic property of the composite structure under investigation.

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