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Interfacially Induced Additional Damping Peaks in Dynamic Mechanical Spectra – Micromechanical Transitions in Multipolymeric Materials

Didier Colombini, Frans H. J. Maurer*

Department of Polymer Science & Engineering, Lund University, Lund Institute of Technology – Box 124, SE – 22100 Lund, Sweden
E-mail: didier.colombini@polymer.lth.se

Summary: The viscoelastic properties of several hypothetical multiphase polymeric materials were investigated in relation to their phase-property dependencies and microstructures. Theoretical mechanical considerations based on the self-consistent interlayer model were performed to point out that specific geometrical arrangements into phases of a set of properties of the pure constituents can lead to interfacially induced damping peaks in dynamic mechanical spectra (DMS). Such additional contributions in DMS were referred to micromechanical transitions to distinguish them from ordinary molecular transitions.

Keywords: additional damping peak, interphase, micromechanical transition, polymer blend, viscoelastic properties

Introduction

The mechanical and viscoelastic properties of multiphase polymeric materials depend on molecular relaxation processes and morphology. Although these relaxations can usually be associated with each component, their appearance also depends on the chemical and physical interactions between the phases. These interactions may evolve in the existence of an interphase, which can lead to an additional damping peak in the dynamic mechanical spectra (DMS) of such multipolymeric systems [1-5]. However, an unexpected additional mechanical transition in DMS does not necessarily reflect an interfacial relaxation process.

Recently, much attention has been focused on predicting the viscoelastic properties of complex polymer systems in relation to their morphologies. As a result, numerous examples of *micromechanical transitions* (MMT) have been reported in the field of particulate multipolymeric systems [6-14]: the origin of such an additional damping peak has been explained by the change in the relative moduli values of the components in the matrix / interphase / particle structure of the multicomponent polymeric materials.

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Basically, it is now well understood that the response of a multiphase polymeric material, to an external force field, is strongly affected by the viscoelastic properties of each component, the interactions between the different phases, the composition, the morphology, and the properties and volume fraction of the interphase. The present work deals with the use of self-consistent mechanical modelling to point out the importance of the microstructure (or geometrical arrangement of phases) and the phase-property-dependence on the viscoelastic damping properties of multipolymeric materials.

Theoretical Considerations – The Interlayer Model [15,16]

The self-consistent interlayer model used in this work, has been extensively described [7,14-16] and requires the definition of a representative volume element (RVE) in order to predict the dynamic mechanical shear and other physical properties of multipolymeric materials. An illustration of a RVE consisting of three concentric spheres embedded in an equivalent homogeneous medium, is depicted in Figure 1.

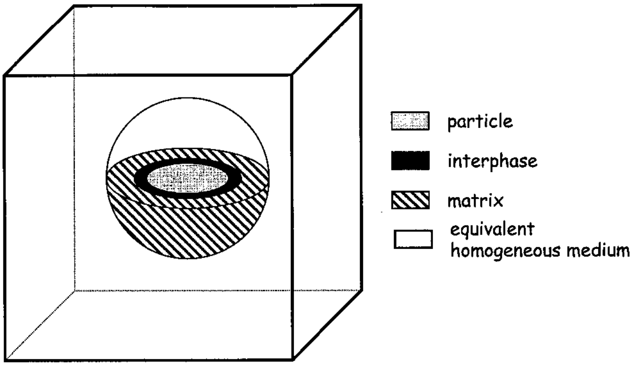

Figure 1: Illustration of a RVE used in the interlayer model

On the one hand, such a geometrical arrangement is representative of the morphology, the particle (phase 1) being surrounded by a shell of interphase (phase 2) which is covered by a shell of matrix (phase 3). On the other hand, the composition of the multicomponent material is also taken into account since the radii of the concentric spheres are chosen in accordance with the volume fractions of the different phases.

Hypothetical Materials

The viscoelastic properties of the hypothetical pure constituents (matrix, interphase, and particle) used as input data in the calculations are given in Figure 2 and Figure 3.

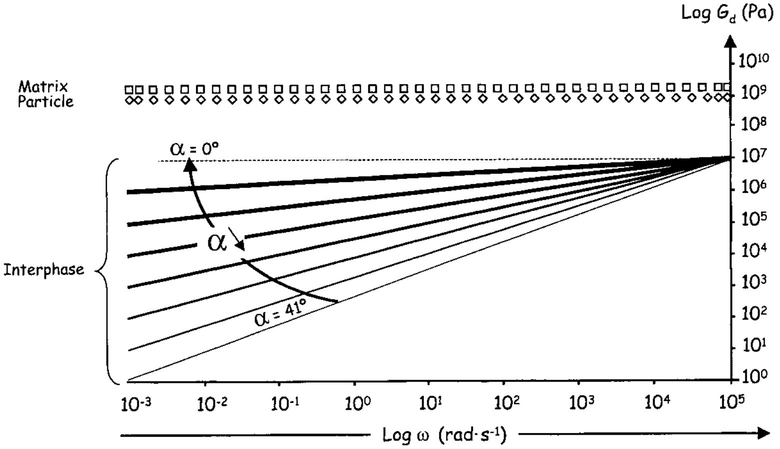

Figure 2: Viscoelastic properties of the hypothetical pure constituents used as input data in the numerical simulations: **dynamic shear modulus (G_d) *versus* frequency** (ω)

The use of isothermal data over a wide frequency range has been thought relevant since both the dynamic shear modulus, G_d, and the phase angle, δ, are frequency (ω) and temperature (T) dependent quantities, and directly related to each other by the following relationship [17]:

$$\delta\,(\omega,T) \approx \frac{\pi}{2}\left|\frac{\partial\ \mathrm{Log}\ G_d(\omega_i,T)}{\partial\ \mathrm{Log}\ \omega_i}\right|_{\omega_i}$$

In agreement with our recent extended investigation [14], both the continuous (matrix) and the dispersed (particle) phase were considered in the calculation to be in the glassy state with constant viscoelastic properties over the whole frequency range. On the same basis [14], their respective Poisson ratios ν_{matrix} and ν_{particle} were kept constant at 0.33.

To point out the interphase-property-dependence of the viscoelastic properties of multipolymeric systems, we decided to perform numerical simulations assuming a significant variation of the dynamic shear modulus of the interphase component. Basically, an angular shift, α, of $G_d^{\text{interphase}}$ has been considered. As illustrated in Figure 2, α is defined as the angle between the dashed line at $G_d^{\text{interphase}}$ equal to 10^7Pa (α = 0°) and the variation of $G_d^{\text{interphase}}$ (from 10^7Pa to 10^x Pa with $x \in [0;6]$). Unless otherwise stated, $\nu_{\text{interphase}}$ was considered constant at 0.5 in calculation.

Worth noting is the absence of a damping peak of any of the pure constituents over the whole frequency range considered (Figure 3).

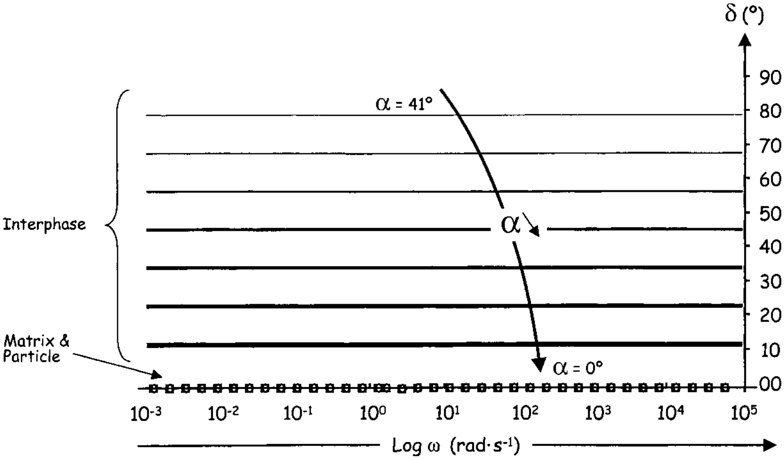

Figure 3: Viscoelastic properties of the hypothetical pure constituents used as input data in the numerical simulations: **phase angle (δ)** ***versus*** **frequency (ω)**

The evolution of α (defined in Figure 2) is highlighted by the arrow.

Results and Discussion

Figure 4 shows the theoretical results obtained for a hypothetical matrix/interphase/particle systems with the same blend composition of 70/5/30 volume parts, respectively. For the entire range of angular shift of $G_d^{interphase}$, the predicted values of both G_d^{blend} and tan δ_{blend} are given versus the frequency. It can be seen in Figure 4 that all the theoretical evolutions of the loss factor present a damping peak.

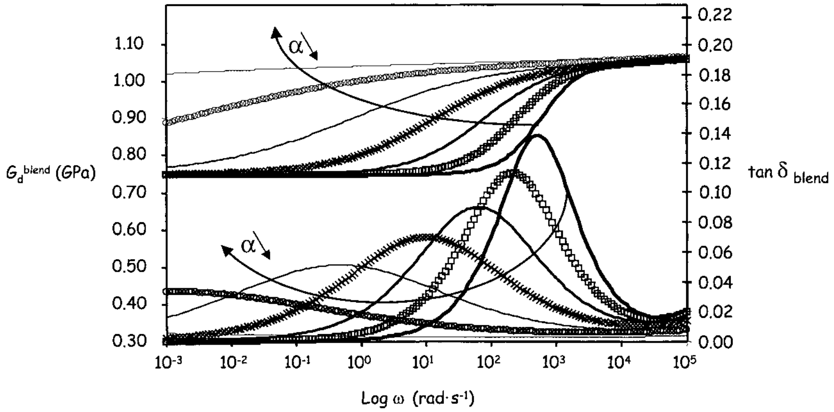

Figure 4: Theoretical viscoelastic properties (G_d and tan δ) of a matrix/interphase/particle (70/5/30) blend *versus* frequency as a function of the angular shift α of $G_d^{interphase}$

The arrow highlights the decrease of α from 41° to 0°.

At the same time as tan δ_{blend} reaches its maximum value, G_d^{blend} drops from a lower level to a higher. It can be noticed that when α decreases:

- the magnitude of the tan δ_{blend} peak decreases and the frequency location of its maximum value is significantly shifted toward lower frequencies,
- the width of the tan δ_{blend} peak increases but,
- the areas under the damping curves remain logically constant since the predicted drops of G_d^{blend} are almost similar.

As the phase angle δ was defined to be constant for each component in the hypothetical blends (see Figure 3), such predicted maxima of tan δ_{blend} have to be related to the change in the relative moduli of the components, since only $G_d^{\text{interphase}}$ was varied in our numerical simulations. In agreement with previous theoretical investigations[7,14], such interfacially induced additional damping peaks in DMS are referred to *micromechanical transitions* (MMT) to distinguish them from other ordinary molecular transitions.

It was then also deemed to be of interest to investigate how a change in either the volume fraction or the Poisson ratio of the interphase component could affect the curves shown in Figure 4. First of all, Figure 5 presents the results of numerical simulations based on matrix / interphase / particle blends with blend compositions of 70/x/30 (x=1,2,5,10 vol. parts) as a function of the dynamic shear modulus of the interphase component (α=41°). The calculated quotients of the dynamic shear modulus of the blend and either that of the matrix or that of the particle are given in Figure 5a. In addition, Figure 5b shows the corresponding values of tan δ_{blend} for the various 70/x/30 blend compositions. Same as in Figure 4, whereas the input data do not include any damping peak over the whole frequency domain considered in the simulations, all the theoretical predictions of the loss factor tan δ_{blend} show a maximum. Moreover, whatever the blend composition, both relative moduli jump from a lower to a higher level (as indicated by the vertical arrows in Figure 5). Similar observations based on the influence of the blend composition on the viscoelastic characteristics of MMT in DMS have been already discussed elsewhere[6-8,14]. On the basis of Figure 5, it can be recalled that:

- the position and magnitude of the jump in the moduli ratios (Figure 5a) as well as the maximum of tan δ_{blend} (Figure 5b), occur at higher $G_d^{\text{interphase}}$ values with increasing volume fraction of the interphase component,
- the more significant the slope in the change of the moduli ratios, the higher the value at the maximum of the tan δ_{blend} peak.

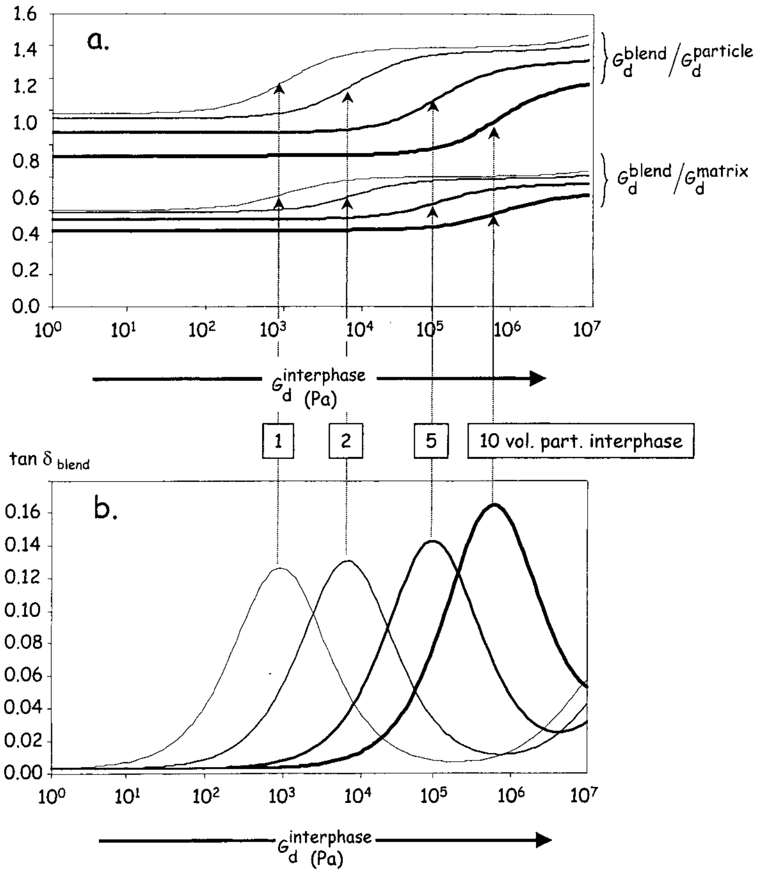

Figure 5: Modelling of the viscoelastic properties of hypothetical matrix / interphase / particle blends

a. (G_d^{blend} / G_d^{matrix}) and (G_d^{blend} / $G_d^{particle}$) versus $G_d^{interphase}$

b. loss factor tan δ_{blend} versus $G_d^{interphase}$

(70/x/30 with x = 1,2,5 or 10 vol. parts, $\nu_{matrix} = \nu_{particle} = 0.33$ *and* $\nu_{interphase} = 0.50$*)*

Finally, Figure 6 shows the results of numerical simulations based on two blend compositions (either 70/5/30 or 70/1/30) for ternary hypothetical matrix/interphase (α=41°)/particle. In order to investigate the influence of $\nu_{interphase}$ on the expected MMT (already observed for $\nu_{interphase}=0.5$, see Figure 5), the numerical calculations were performed by considering either $\nu_{interphase}=0.5$ or $\nu_{interphase}=0.499$. On the basis of previous investigations[7,14], ν_{matrix} and $\nu_{particle}$ were kept constant at 0.33. Basically, the way to present the predicted viscoelastic data in connection with the properties of the interphase component is similar in Figure 6 to that of Figure 5. It can be seen (Figure 6b) that the position of the maximum of tan δ_{blend} appears to be really sensitive to the changes of $\nu_{\text{interphase}}$ from 0.5 to 0.499. Nevertheless, such an amazing observation is significantly dependent on the volume fraction of the interphase, since the observed changes (Figures 6a and 6b) are much more significant for the 70/1/30 blend than for the 70/5/30 system. In any cases, such a noticeable influence of $\nu_{\text{interphase}}$ strongly indicates that the compressibility of the interfacial layer in a ternary polymer blend substantially affects the overall viscoelastic response of the multicomponent material.

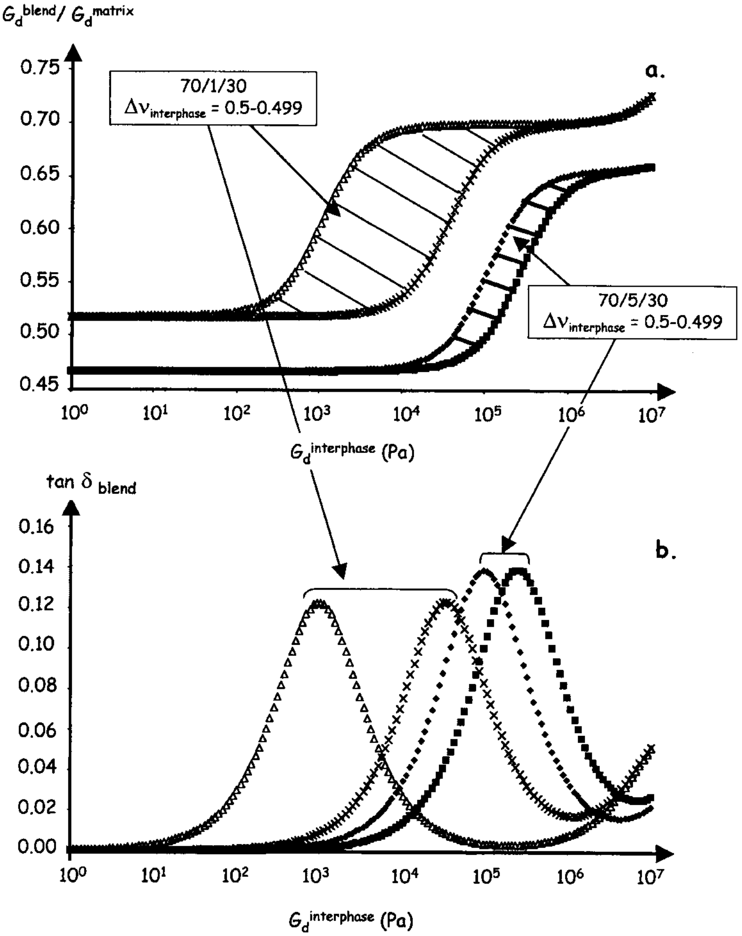

Figure 6: Modelling of the viscoelastic properties of hypothetical matrix / interphase / particle blends (70/5/30 or 70/1/30). **Composition dependence of the theoretical influence of $\nu_{\text{interphase}}$** ($\nu_{\text{interphase}}$ = 0.5 or 0.499)

a. (G_d^{blend} / G_d^{matrix}) versus $G_d^{\text{interphase}}$

b. tan δ_{blend} versus $G_d^{\text{interphase}}$

Conclusion

This work was mainly based on the use of the interlayer model to demonstrate the importance of the microstructure (or geometrical arrangement of the phases) and the phase-property-dependence on the overall viscoelastic damping properties of multipolymeric materials. Such a theoretical investigation based on self-consistent mechanical modelling can be reasonably considered as relevant arguments to justify the existence of "spurious" additional damping peaks in some experimental DMS reported in the literature for multipolymeric materials. Thus, it was emphasised that in some cases, a specific geometrical arrangement into phases of a set of properties of the pure constituents (none of them including any loss peak), can lead to an interfacially induced damping contribution in DMS. Such a phenomenon, so-called *micromechanical transition* definitively differs from classical molecular transitions, which solely reflect the molecular relaxation of macromolecules. Especially, it might be kept in mind that a MMT is an indicator of the manifestation of the interfacial area in a multicomponent polymeric system (the compressibility of which strongly influences the viscoelastic characteristics of the MMT in DMS), since this phenomenon requires the presence of a specific interphase, whose properties affect the overall relative moduli of the blended material and its components.

Acknowledgements

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[1] L.A. Utracki, "*Polymer Alloys and Blends – Thermodynamics and Rheology*", Hanser Verlag Publishers: Munich, Vienna, New York, **1989**
[2] S.W. Shalaby, "*Thermal Characterisation of polymeric materials*", Turi, E. A., Ed., Academic Press: London, **1981**
[3] Y.S. Lipatov, F.G. Fabulyak, V.V. Shifrin, *Polym. Sci. USSR* **1976**, 18, 866
[4] J.L. Thomason, "*Interfaces in Polymer, Ceramic and Metal Matrix Composites*", Ishida, H., Ed.; Elsevier Science: New York, **1988**
[5] L.T. Drzal, *Adv. Polym. Sci.* Ser. No 75, **1986**
[6] H. Eklind, S. Schantz, F.H.J. Maurer, P. Jannasch, B. Wesslen, *Macromolecules*, **1996**, 29, 984
[7] H. Eklind, F.H.J. Maurer, *Polymer*, **1996**, 37, 2641
[8] H. Eklind, F.H.J. Maurer, *Polym. Sci., Phys. Ed.*, **1996**, 34, 1569
[9] C.O. Hammer, F.H.J. Maurer, *Polymer*, **1998**, 39, 4243
[10] D. Colombini, J.J. Martinez-Vega, G. Merle, E. Girard-Reydet, J.P.P. Pascault, J.F. Gerard, *Polymer*, **1999**, 40, 935
[11] D. Colombini, G. Merle, N.D. Alberola, *J. Macromol. Sci. - Physics*, **1999**, B38 (5&6), 957
[12] D. Colombini, G. Merle, N.D. Alberola, *Macromol. Symp.*, **2001**, 169, 235
[13] D. Colombini, G. Merle, N.D. Alberola, *Macromolecules*, **2001**, 34, 5916
[14] D. Colombini, F.H.J. Maurer, *Macromolecules*, **2002**, 35, 5891
[15] F.H.J. Maurer, "*Polymer Composites*", Sedlacek, B., Ed.; W. de Gruyter & Co: Berlin, **1986**, 399
[16] F.H.J. Maurer, "*Controlled Interphases in Composite Materials*", Ishida, H., Ed.; Elsevier Science: New York, **1990**, 491
[17] H.C. Booij, G.P.J.M. Thoone, *Rheol. Acta*, **1982**, 21,15