RHEOLOGICAL BEHAVIOUR OF HIGH-VISCOSITY EMULSIONS: A COMPARISON BETWEEN THE PREDICTIVE CAPABILITIES OF SEVERAL THEORETICAL MODELS

J. M. Silva, A. V. Machado and J. M. Maia*

Department of Polymer Engineering ,
University of Minho, Campos de
Azurém, 4800 Guimarães, Portugal,
email: jmaia@dep.uminho.pt

Keywords: Emulsions models; polymer blends; linear viscoelastic behaviour.

Synopsis

Several models (Palierne, Bousmina (1999) and Lee-Park models) for describing the rheological behaviour of emulsions of polymers are compared. For characteristic values of blends of immiscible polymers, the Palierne and Bousmina models give predictions approximately similar for linear viscoelastic data. The Doi-Otha and Lee-Park models are able, in principle, to describe the behaviour of polymer blends for any type of flow and are usually used to predict the transient response of emulsions. In this work we compare the Lee-Park model and an extension of the Doi-Otha model to include fluids with different viscosities with the Palierne model for linear viscoelastic proprieties.

INTRODUCTION

In last years, the importance of blends of immiscible polymers has increased with a large number of studies about relationships between rheology and morphology having been developed. In fact, the rheological behaviour of a blend depends not only on the properties and proportion of the neat polymers, but also on its morphology and the interfacial tension between polymers. Palierne derived an equation for predicting the molten immiscible polymer blend behaviour when subject to small amplitude oscillatory flow:

$$G_B^{¿}=\frac{1+3\sum_i \square\, \phi_i H_i^{¿}(\omega)}{1-2\sum_i \square\, \phi_i H_i^{¿}(\omega)}G_M^{¿}(\omega)$$

(1)

with

$$H_i^{¿}(\omega)=\frac{4(\alpha/R_i)\left[2G_M^{¿}(\omega)+5G_I^{¿}(\omega)\right]+\left[G_I^{¿}(\omega)-G_M^{¿}(\omega)\right]\left[16G_M^{¿}(\omega)+19G_I^{¿}(\omega)\right]}{40(\alpha/R_i)\left[G_M^{¿}(\omega)+G_I^{¿}(\omega)\right]+\left[2G_I^{¿}(\omega)+3G_M^{¿}(\omega)\right]\left[16G_M^{¿}(\omega)+19G_I^{¿}(\omega)\right]}$$

(2)

where $G_M^{¿}$ is complex modulus of the matrix, $G_I^{¿}$ is complex modulus of the dispersed phase, α is the interfacial tension and ϕ_I is the volume fraction of particles with radius R_i.

Starting from the Kerner model, Bousmina derived another expression for $G^{¿}$

$$G_B^{¿}=G_m^{¿}\frac{2\left(G_I^{¿}+\alpha/R\right)+3G_M^{¿}+3\phi\left(G_I^{¿}+\alpha/R-G_M^{¿}\right)}{2\left(G_I^{¿}+\alpha/R\right)+3G_M^{¿}-2\phi\left(G_I^{¿}+\alpha/R-G_M^{¿}\right)} \quad (3)$$

where R is the mean radius of dispersed phase.
A new model was proposed for Doi and Otha and later modified by Lee and Park to account for a mismatch in the viscosities of polymers. They proposed the following constitutive equation:

$$\sigma_{ij}=\left(1+\frac{6\left(\eta_I-\eta_M\right)}{10\left(\eta_I+\eta_M\right)}\phi\right)\eta_M\dot{\gamma}_{ij}-\alpha q_{ij}-P\delta_{ij} \quad (4)$$

where the anisotropy tensor is given by

$$\frac{\partial}{\partial t}q_{ij}=-q_{ik}d_{kj}-q_{jk}d_{ki}+\frac{2}{3}\delta_{ij}d_{lm}k_{lm}-\frac{Q}{3}\left(d_{ij}+d_{ji}\right)+\frac{q_{lm}d_{lm}}{Q}q_{ij}-\lambda\frac{\alpha}{\eta_M}Qq_{ij}-\lambda\nu\frac{\alpha}{\eta_M}\left(\frac{q_{lm}q_{lm}}{Q}\right)q_{ij} \quad (5)$$

$$\frac{\partial}{\partial t}Q=-d_{ij}q_{ij}-\lambda\mu\frac{\alpha}{\eta_M}Q^2-\lambda\nu\frac{\alpha}{\eta_M}q_{ij}q_{ij} \quad (6)$$

where λ is total relaxation parameter, μ size relaxation, ν shape relaxation. The μ parameter is associated to coalescence, so, it can be considered zero in small amplitude oscillatory flow because deformation of dispersed phase is small. Other considerations suggested $\nu=1-\phi$, for the same flow type.

INFLUENCE OF EMULSION PARAMETERS IN THE PALIERNE MODEL

We considered a two fluids emulsion. We suppose that both fluids behaviour of Maxwellian mode, according to

$$G^{¿}=\frac{i\omega\eta}{1+i\omega\lambda} \quad (7)$$

with $\lambda_M=\lambda_I=0.1\ s$. We suppose that: matrix and inclusions have the same viscosity ($\eta_M=\eta_I=10^6$ Pa.s), the interfacial tension is $10\,mN/m$, the volume fraction is 0.2 and all droplets have same radius, $R=1\mu\ m$. Then, we change some parameters value.

A. Radius of dispersed phase

Figure 1 show that the plateau modulus in $G^{''}$ decrease with increasing of radius of particles of dispersed phase. The effect of interfacial tension is opposite since eq 2 depends on α / R_i.

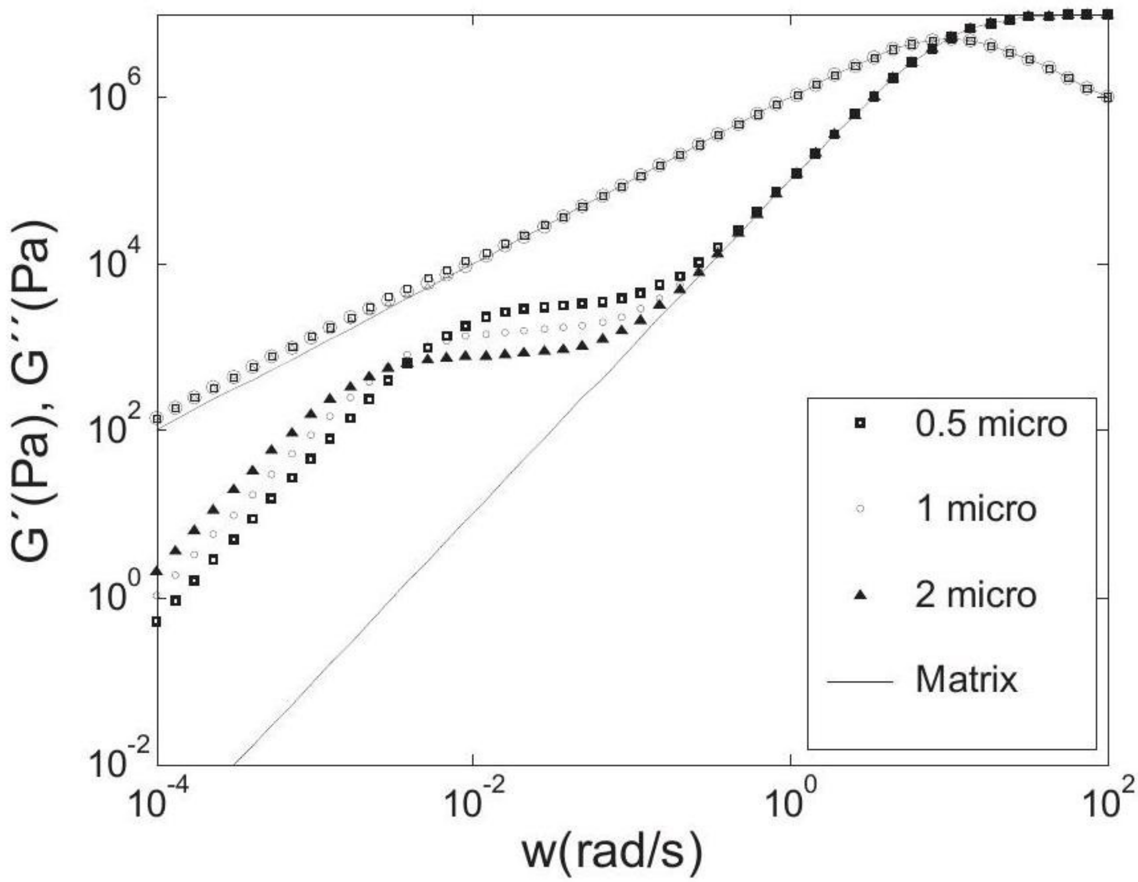

Figure 1 - Dynamic moduli vs frequency. Effect of variation of radius of inclusions. (micro ¿ μm)

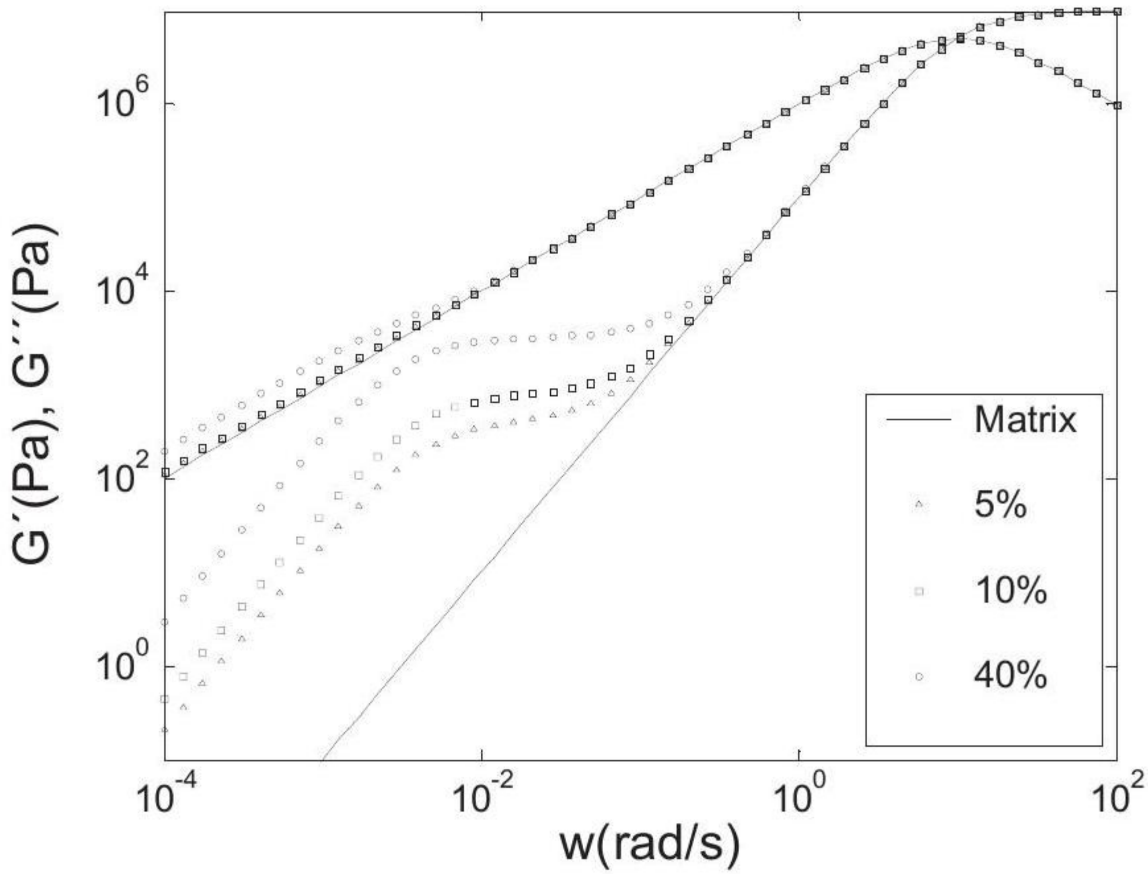

Figure 2 - Dynamic moduli vs frequency. Effect of variation of volume fraction of disperse phase.

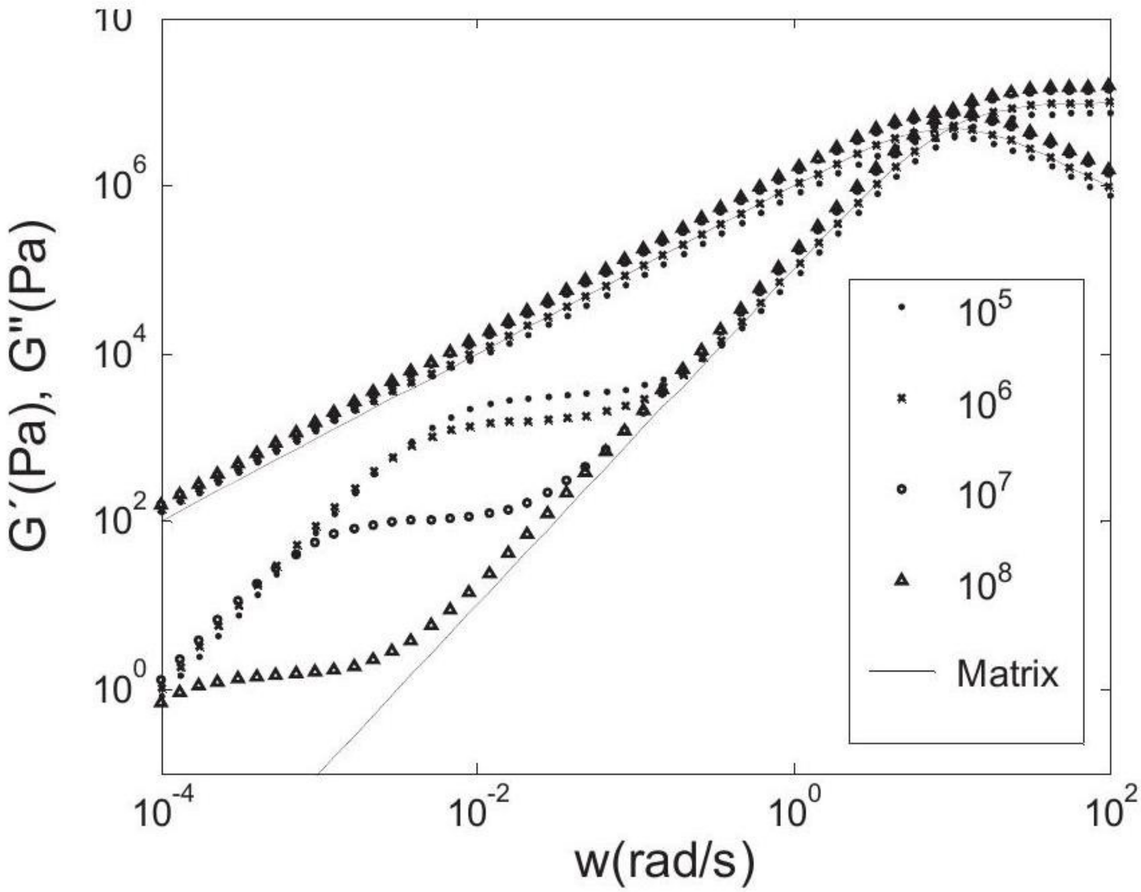

Figure 3 - Dynamic moduli vs frequency. Effect of the zero-shear viscosity of the dispersed phase.

B. Volume fraction of the dispersed phase

The increase of volume fraction of dispersed phase leads to an increase of the G'' plateau; figure 2 also shows a slight increase of G''' to low frequencies.

Viscosity ratio

From the analysis of figure 3 we conclude that plateau modulus in G'' decreases with increasing of viscosity ratio between the dispersed phase and the matrix.

Relaxation time of the dispersed phase

When the relaxation time of the dispersed phase increases the plateau modulus in G'' also increases (Figure 4).

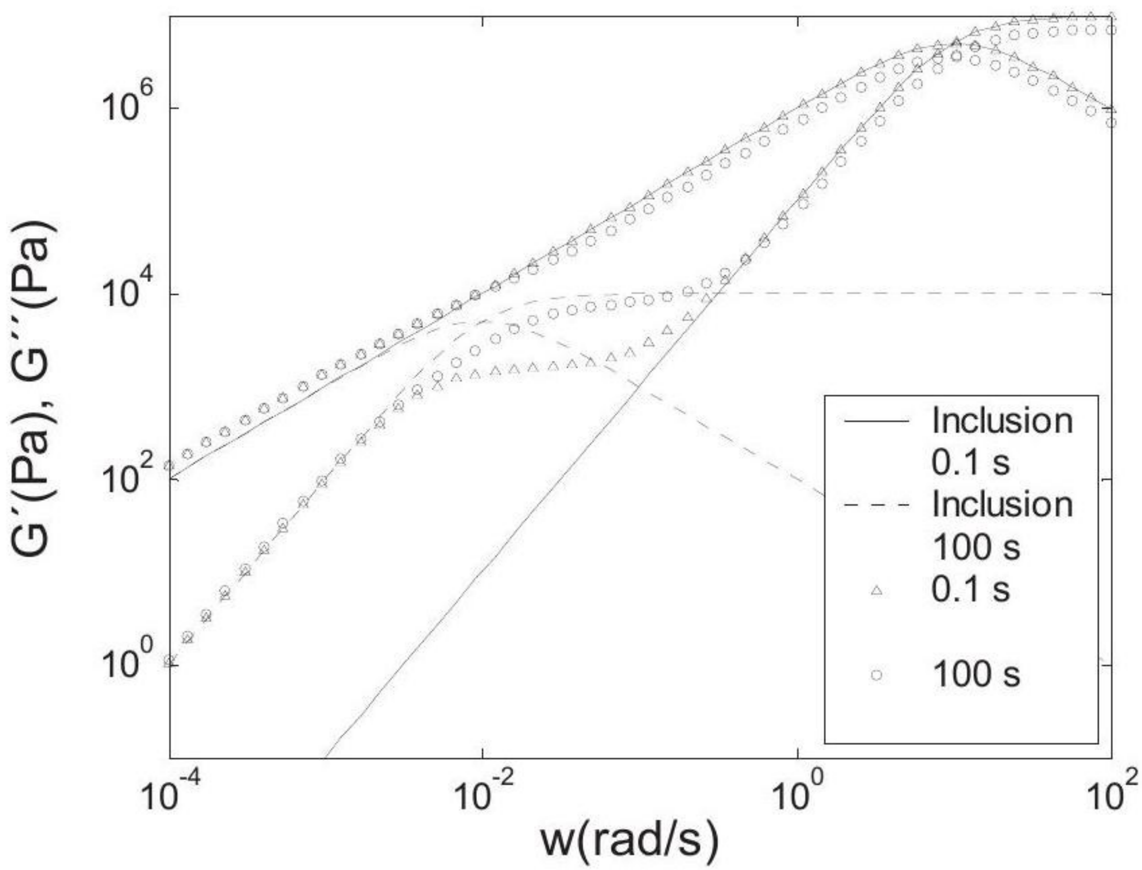

Figure 4 - Dynamic moduli vs frequency. Effect of relaxation time of dispersed phase.

III.COMPARISON BETWEEN PALIERNE AND LEE-PARK MODELS

The Bousmina and Palierne models give very similar predictions for typical values of the parameters, which is not the case with the predictions of the Lee-Park model. We compared these models varying different parameters.

A. Radius

In the Lee-Park model the interfacial area, Q, appears and is related to the particle radius by:

$$Q = \frac{6\phi}{R} \quad (8)$$

Figure 5 shows, for both radii, that the plateau modulus in G'' predicted for by the Lee-Park model is higher than that predicted by Palierne model.

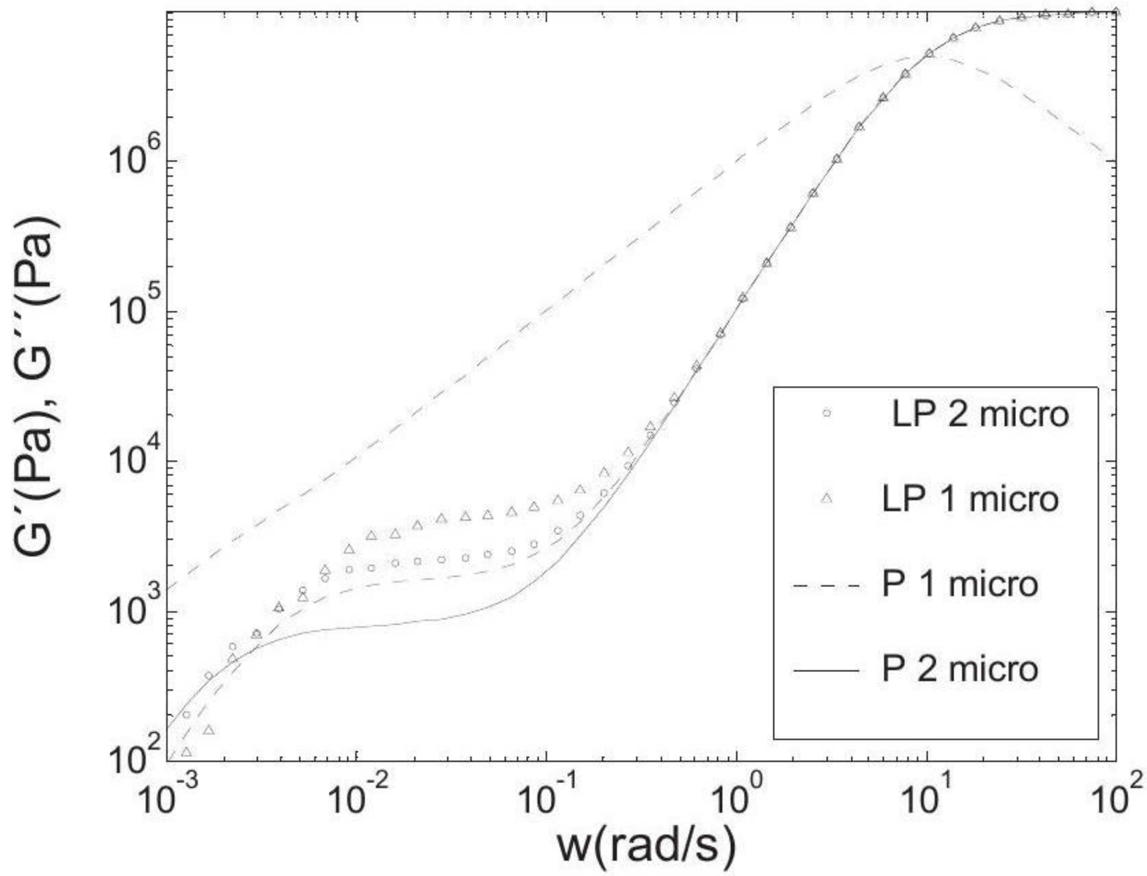

Figure 5 - Dynamic moduli vs frequency. Comparation of models predictions for different radius of inclusions. (micro ¿ μm, PL- Lee-Park model, P- Palierne model, $\lambda = 0.6$)

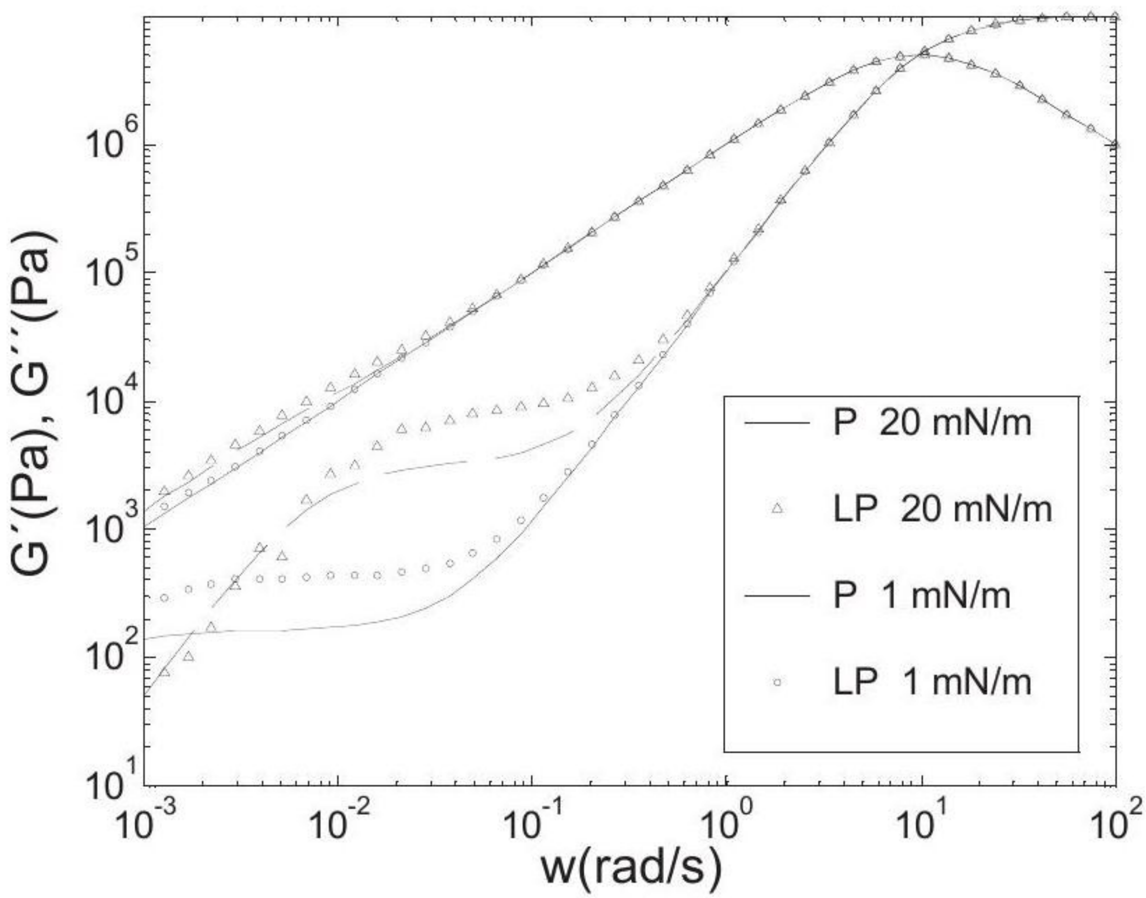

Figure 6 - Dynamic moduli vs frequency. Comparation of models predictions for different values of interfacial tension. (PL- Lee-Park model, P- Palierne model, λ=0.6)

B. Interfacial tension

The Lee-Park model predicts a higher value for plateau in $G^{''}$, for different values of interfacial tension (Figure 6).

Another parameters

The Lee-Park model shows low sensibility to variations of viscosity ratio and volume fraction of dispersed phase.

CONCLUSIONS

The Palierne and Bousmina models give quantitatively similar predictions for $G^{''}$ and $G^{'''}$ of blends in small amplitude oscillatory flows. The Doi-Otha family of models, on the other hand, present an great advantage: they can, in principle, be used for predict behaviour of
a blend in any type of flow, namely, in transient experiences. The Lee-Park model

is applicable to blends with any viscosity ratios and predicts higher values for the plateau in G'' than the Palierne model.

References

Palierne, J. F. (1990). "Linear Rheology of Viscoelastic Emulsions with Interfacial-Tension." Rheol Acta 29(3): 204-214

Doi, M. and T. Ohta (1991). "Dynamics and Rheology of Complex Interfaces .1." J Chem Phys 95(2): 1242-1248

Lee, H. M. and O. O. Park (1994). "Rheology and Dynamics of Immiscible Polymer Blends." J Rheol 38(5): 1405-1425

Lacroix, C., M. Aressy, et al. (1997). "Linear viscoelastic behavior of molten polymer blends: A comparative study of the Palierne and Lee and Park models." Rheol Acta 36(4): 416-428

Bousmina, M. (1999). "Rheology of polymer blends: linear model for viscoelastic emulsions." Rheol Acta 38(1): 73-83

Graebling, D., R. Muller, et al. (1993). "Linear Viscoelastic Behavior of Some Incompatible Polymer Blends in the Melt - Interpretation of Data with a Model of Emulsion of Viscoelastic Liquids." Macromolecules 26(2): 320-329