e-Polymers **2007**, no. 129

http://www.e-polymers.org
ISSN 1618-7229

Novel results and potential applications of bitumen used as an additive for polyethylene

Goretti Goikoetxeaundia,[1] Alexander Mateos,[1] Oscar González,[1] María Eugenia Muñoz,[1] Anton Santamaría[1] and Inmaculada Martínez[2]*

[1*]Department of Polymer Science and Technology. POLYMAT. University of The Basque Country. P.O. Box 1072. San Sebastian (Spain); fax: +34 943 015270; email: antxon.santamaria@ehu.es
[2]Department of Chemical Engineering, Faculty of Experimental Science, Campus "El Carmen", University of Huelva, 21071 Huelva (Spain); fax: +34 959 219983; email: imgarcia@uhu.es

(Received: 16 May, 2007; published: 7 November, 2007)

Abstract: A metallocene catalysed linear low density polyethylene (mLLDPE) was mixed with very low amounts of bitumen (1-2%) as an additive. Bitumen interacts with mLLDPE giving rise to a dying effect, which turns the originally white mLLDPE extrudates into black. No slippage is observed during extrusion and sharkskin is postponed as bitumen is added. "Melt strength" values of the blends, determined in melt spinning experiments, are very similar to those of mLLDPE. Accordingly good performance is expected in film-blowing process. Tensile modulus values are higher than 10^9 Pa. Bitumen emerges as an alternative to carbon black powder currently used to obtain black polymer films.

Introduction

Bitumen/polymer blends have been quite extensively investigated, because they are employed for road paving and waterproofing membranes. Blends utilized in road paving posses a proportion of bitumen close to 95%, which leads to a bitumen continuous phase reinforced by polymer particles that improve viscoelastic properties [1]. On the other hand, roof membranes are based typically on 85% bitumen/15% polymer blends. Bitumen can be fractionated into four fractions: saturates, aromatics, resins and asphaltenes. The three first fractions constitute the maltene phase. The interaction of the polymer with maltene (in particular with saturated oils) leads to constitute a polymer-rich continuous phase which contributes decisively to impart good physical properties to the membranes [2].

Turning the current framework of bitumen/polymer blends upside down, the use of very small amounts of bitumen to modify the properties of polymers has not been contemplated at all, although it poses new academia and industrial challenges. Aiming to develop new applications for bitumen, the possibility of using this natural polymer as a black dye for thermoplastics is considered in this work. For this purpose, mixtures of a metallocene catalysed linear low density polyethyelene (mLLDPE) with conventional paving grade bitumen, are investigated.

Results and discussion

The physical behaviour of the blends is marked by a certain chemical affinity of the polymer with the saturated oils of the bitumen. As has been reported in the literature, this is a consequence of the proximity of the solubility parameter values of mLLDPE, Δ = 15.8-18.0 $(MPa)^{0.5}$ [3], and saturated resins Δ = 17.4 $(MPa)^{0.5}$ [4]. The so called Mavridis-Shroff plots [5], phase angle δ *versus* complex modulus G^* at different temperatures, configure a reliable method to analyse thermorheological complexity of polymer systems [6]. The data displayed in Figure 1 show a simple thermorheological behaviour, as time-temperature superposition holds in the investigated temperature range (145-190 ºC). Although this result is not definitely conclusive, it constitutes a hint of miscibility.

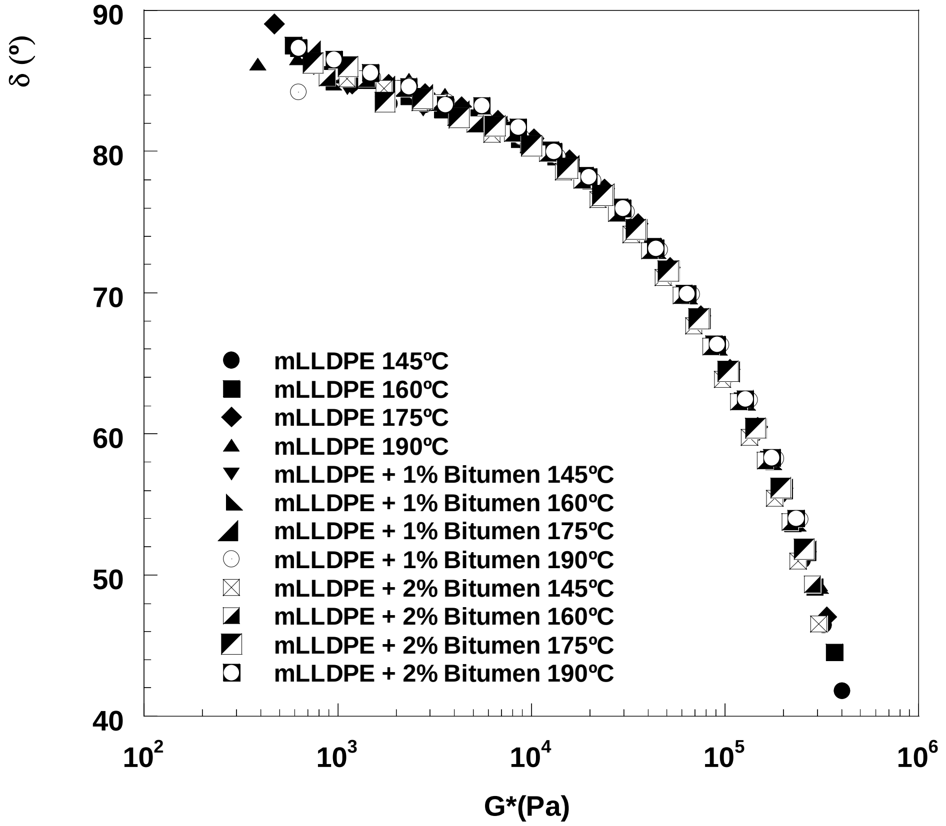


Fig. 1. Mavridis and Shroff criterion to investigate thermorheological complexity of the blends (see text).

Besides the chemical affinity between the components, the extremely low viscosity of the bitumen (Fig. 6) favours its diffusion in the polymer matrix. Considering both, chemical and rheological effects, it can be deduced that during the measurements in the extrusion capillary rheometer the bitumen tends to diffuse to the surface. This gives rise to a dying effect which is noticed in Figure 2: a very small amount of bitumen (2%) is capable of giving a black colour to the originally white mLLDPE extrudates.

Interestingly enough, we observe that extrudates are perfectly dyed, with not at all symptoms of exudation. That is to say, the bitumen diffuses in the polymer matrix, but does not reach to leave to the outside. As it is shown below, this result opens the door to an alternative to carbon black powder currently used to obtain black polymer films employed in low parts of agriculture greenhouses.

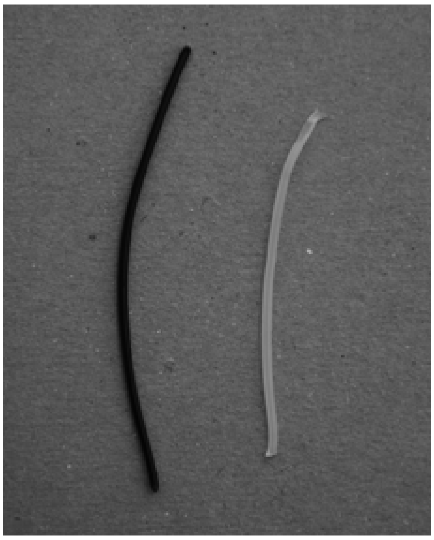


Fig. 2. Photograph showing the dying effect of 2% bitumen on originally white mLLDPE extrudate.

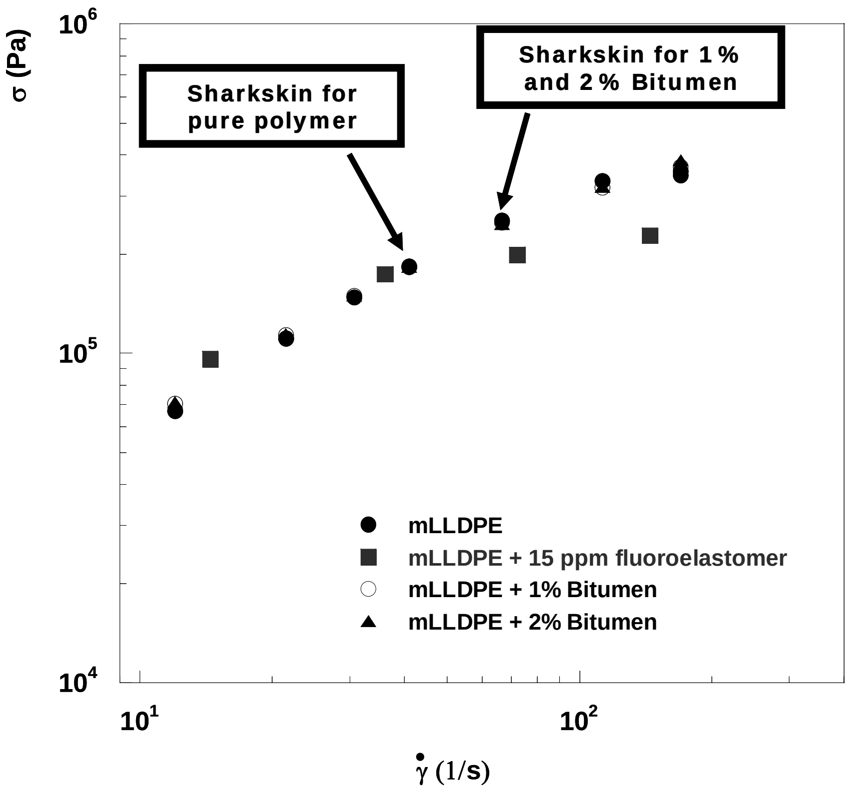
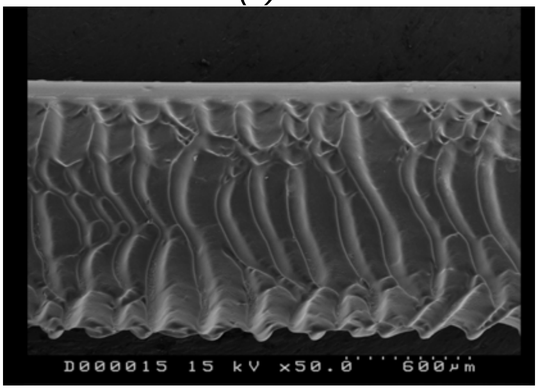


Fig. 3. Flow curves of pure mLLDPE and its blends. The flow curve of mLLDPE with a processing aid fluoroelastomer (mLLDPE-15 ppm fluoroelastomer) is included for comparison purposes. The arrows indicate the onset of sharkskin; as expected, no such flow instability is observed with mLLDPE-15 ppm fluoroelastomer sample.

In Figure 3 flow results of mLLDPE with a processing aid fluoroelastomer are included for comparison purposes: the different role played by the bitumen and the processing aid agent is evident. Notwithstanding the incapacity of the bitumen to diminish shear stress, the reduction of the severity of sharkskin flow instability is noticeable in Figure 5.

(a)



(b)

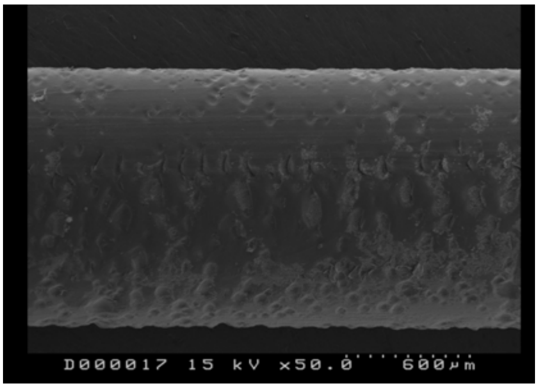


Fig. 4. Microphotographs of extrudate obtained at a shear rate $\dot{\gamma}_{21}$= 66.56 s^{-1}. Sharkskin flow instability is not practically noticeable for mLLDPE/2% bitumen blend. a) mLLDPE, b) mLLDPE/2% bitumen blend.

In particular the critical shear rate for the onset of sharkskin (marked in Figure 3) is postponed, from $\dot{\gamma}_c$ =35 s^{-1} (pure mLLDPE) to $\dot{\gamma}_c$= 70 s^{-1} for mLLDPE with 1% bitumen. This is an encouraging result, since the development of sharkskin at shear rates involved in polymer extrusion (close to 100 s^{-1}) limits the industrial use of metallocene catalysed LLDPEs. Nowadays it is generally accepted that sharkskin is originated by a tearing or cracking at the surface of the extrudate, caused by elongational flow at the exit of the die [7-8]. Slippage of the polymer melt along the capillary wall, provoked typically by a processing aid agent, reduces very significantly elongational flow at the exit, avoiding sharkskin [9]. According to the results shown in Figure 3, no slippage is noticed in our mLLDPE / bitumen mixtures, which leads us to assume that this is not the cause of the observed sharkskin mitigation. Assuming that a tearing of the extrudate is the original cause of sharkskin, Rutgers and Mackley [10] conclude that the onset of this instability is shifted to higher shear rates, as the “melt stress” (stress at filament breakage, determined in a melt spinning experiment) increases. The melt spinning results of pure mLLDPE and its blends with bitumen are displayed in Figure 5.

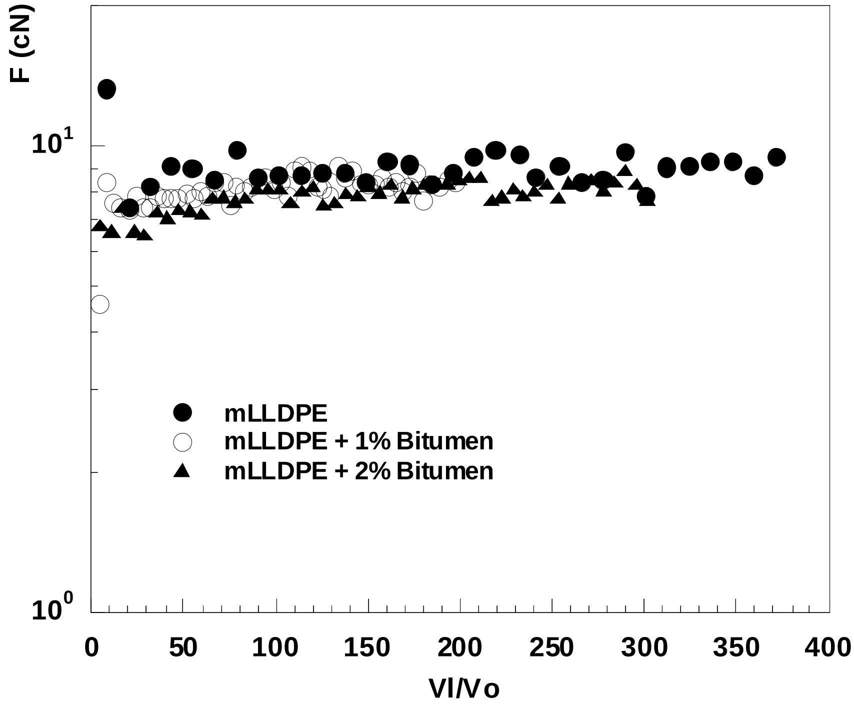


Fig. 5. Melt spinning results of pure mLLDPE and its blends: stretching force is plotted against stretching drawdown ratio.

Quite similar results are obtained for pure mLLDPE and its blends, although stretch ratio at breaking, $(Vl/Vo)_M$, data are somewhat uncertain. In any case, no higher melt strength values can be observed for the mixtures, discarding the hypothesis of Rutgers and Mackely as being the cause of sharkskin mitigation. Therefore, the reason for sharkskin reduction by using bitumen is still unknown. A deeper analysis of this result is necessary; notwithstanding this is out of the scope of this paper.

One of the most important applications of the metallocene catalysed polyetheylenes is the production of films by extrusion-blowing process. In particular our mLLDPE sample corresponds to this grade of polyethylenes. Melt spinning results are linked to film-blowing process of polyethylenes [11]. Actually, the continuity of the process requires good bubble stability, which is improved as the “melt strength” (breaking force in melt spinning experiments) of the polyethylene increases. It has also been observed that the larger the melt elasticity of the polyethylene, the more stable is the bubble [12]. Melt elasticity of our samples can be inferred from the data presented in Figure 1: the samples are more elastic as the complex modulus G^* becomes higher and the phase angle δ lower. The melt elasticity (Figure 1) and melt spinning data (Figure 5) indicate that the inclusion of small amounts of bitumen does not alter the results of pure mLLDPE. A practical conclusion of this outcome is that a priori mLLDPE / bitumen films could be made by extrusion-blowing process under conditions similar to those of pure mLLDPE.

The results of the tensile elastic modulus E' as a function of frequency at room temperature are presented in Figure 6. A certain modulus reduction is observed as bitumen is added to pure polyethylene, although, in any case, E' remains above 10^9 Pa.

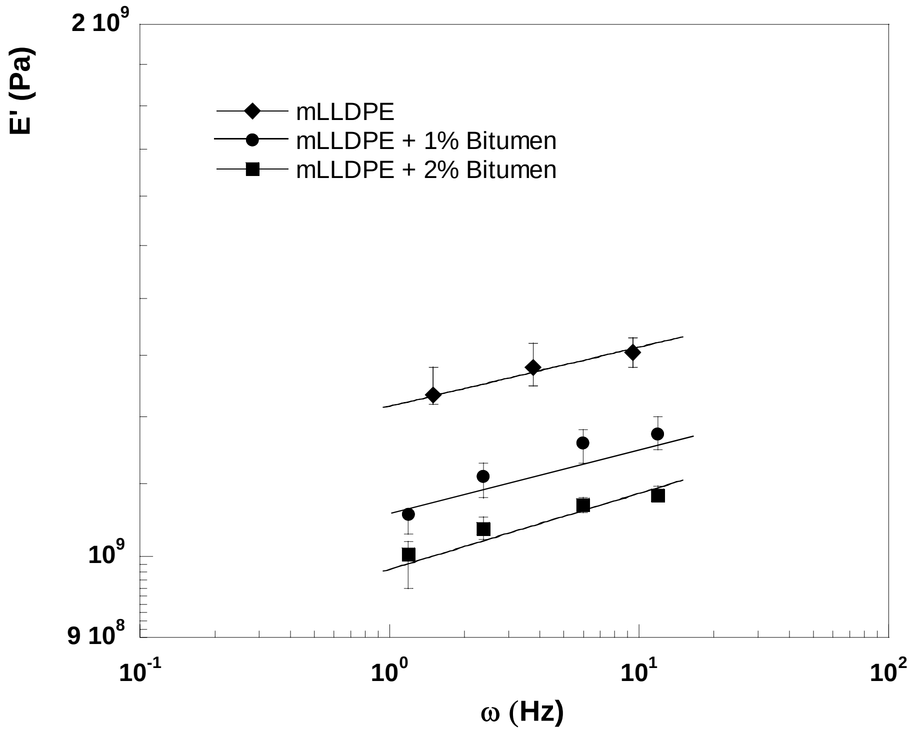


Fig. 7. Tensile elastic modulus as a function of frequency at T=23 ºC.

Conclusions

Bitumen interacts with metallocene catalysed linear low density polyethylene and diffuses in the polymer matrix, giving rise to a dying effect. Accordingly, a very small amount of bitumen (2%) is capable of turning into black colour originally white mLLDPE extrudates: these are perfectly dyed and do not exude.

Extrusion flow results of pure mLLDPE and 1% and 2% bitumen mixtures show that, although shear stress is not reduced by the presence of bitumen, sharkskin instability (typical of metallocene polyethylenes) is postponed to higher shear rates. Melt spinning experiments, originally considered to be linked with sharkskin results, give very similar "melt strength" values for pure mLLDPE and the blends. A good performance is expected in film-blowing process, according to melt spinning results. Notwithstanding a certain reduction of the tensile modulus is observed for 1% and 2% bitumen mixtures, E' values are above 10^9 Pa.

Our results show that bitumen can be used as a black dye for polyethylene, offering the advantage of a cheaper and cleaner product than carbon black powder currently used in industry.

Experimental part

Materials and blends preparation

The weight average molecular weight M_w and the number average molecular weight M_n of the mLLDPE sample are, respectively, 118000 and 55000 g/mol. The technical characteristics of the bitumen are: penetration degree 160/220, ring-ball temperature 43 ºC and asphaltene content 20.9%.

Blends of 1 and 2% bitumen content were prepared in a Mini Max Molder (CS-183MMX) at *T*= 170 ºC.

Rheological measurements

Shear and elongational flow measurements were carried out in a CEAST 5000 Capillary Rheometer equipped with a stretching unit. Shear viscosity was determined at *T*=190 ºC and elongational measurements (Tensile force *versus* stretching ratio in melt spinning experiments) were carried out under non-isothermal conditions. Complementary experiments were also performed in torsion mode (Couette flow) in Physica Rheolab equipment. Dynamic viscoelastic functions (Elastic modulus *G´*, Viscous modulus *G´´*, phase angle δ and complex modulus *G**) were evaluated using a plate-plate geometry in a ARES Rheometer (TA Instruments) at temperatures ranging from 145 º to 190 ºC. The tensile properties of the filaments obtained in melt spinning experiments were analysed in the ARES Rheometer using the fiber and film tension geometry.

The mixing process, as well as rheological measurements, were both carried out at temperatures close to *T*=180 ºC, temperature at which the viscosity of the bitumen is hundred times lower than that of mLLDPE, as can be seen in Figure 7.

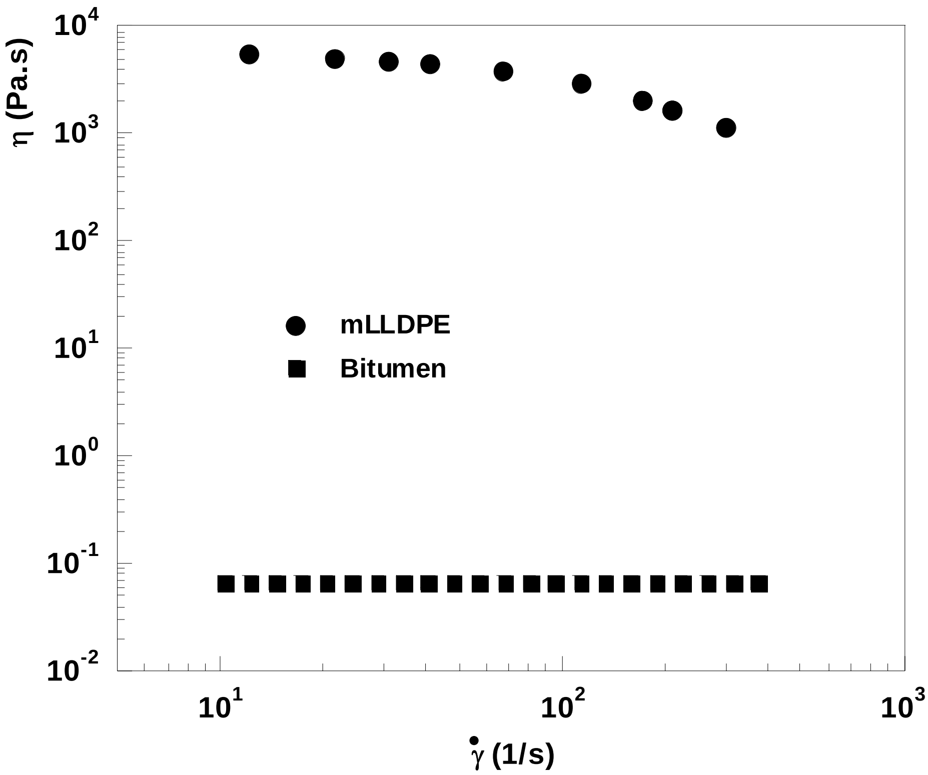


Fig. 7. Viscosity as a function of shear rate determined at 190 ºC in Couette flow.

Acknowledgements

Financial support through MEC (MAT2004-06299-C02-01) (Spanish Government) and UPV/EHU (00203.215-14498/2002) (University of The Basque Country) is acknowledged.

References

[1] Read, J. *Chemistry in Britain* **1998**, 34, 46-49.
[2] Goikoetxeaundia, G.; González, O.; Muñoz, M.E.; Peña, J.J.; Santamaría, A. *Macromol. Mater. Eng.* **2007** (accepted).
[3] Graesley, W.W. *Polymer liquids and networks: structure and properties.* New York: Garlan Science; **2004**.
[4] Hagen, A.P.; Jones, R.;Hofener, R.M.; Rabdolph, B.B.; Johnson, M.P. *Proc. Assoc. Asphalt Paving Technol.* **1984**, 53, 119-137.
[5] Mavridis, H.; Shroff, R.N. *Polym. Eng. Sci*. **1992**, 32, 1778.
[6] Zárraga, A.; Peña, J.J.; Muñoz, M.E.; Santamaría, A. *J. Polym. Sci. Polym. Phys.* **2000**, 38, 469-477.
[7] Cogswell, F.N. *J Non-Newtonian Fluid Mech* **1977**, 2, 37.
[8] Migler, K.B.; Lavallée, C.; Dillon, M.P.; Woods, S.S.; Gettinger, C.L. *J.Rheol.* **2001**, 45, 565.
[9] Piau, J.M.; El Kissi, N.; Toussaint, F.; Mezghani, A. *Rheol. Acta* **1995**, 34, 40.
[10] Rutgers, R.; Mackley, M. *J. Rheol*. **2000**, 44, 1319.
[11] Pérez, R.; Rojo, E.; Fernández, M.; Leal, V.; Lafuente, P.; Santamaría, A. *Polymer* **2005**, 46, 8045-8053.
[12] Fang, Y.; Lafleur, P.G.; Carreau, P.J. *Polym.Eng. Sci.* **2003**, 43, 1391.