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The role of a dechlorinated PVC as compatibiliser for PVC/polyethylene blends

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Summary

Reductive dechlorination of PVC was carried out to obtain a compatibiliser for PVC/polyethylene blends. The performance of this modified PVC is compared with the compatibilising effect of a random chlorinated polyethylene copolymer, analyzing morphology as well as rheological and mechanical properties.

Introduction

Polyethylene and PVC differ in many aspects making them difficult to blend together. Large contrasts in polarity, crystallinity and viscosity, together with the presence of microcrystallytes in the molten state, lead to incompatibility. During mixing, a domain structure with a low adhesion between phases is generated. This gives rise to poor mechanical properties which limit the practical use of the blends of two of the most widely utilized polymers. As in the case of other incompatible polymers, the addition of a third component which "compatibilises" the blend, as it improves its mechanical properties constitutes a route, which has given good results.

The work of Schramm and Blanchard [1] was a pioneering contribution for the use of chlorinated polyethylene (CPE) to improve the properties of PVC/PE blends. The solid-state procedure developed by these authors to chlorinate polyethylene leads to a multiblock copolymer with polyethylene segments and blocks similar to PVC. This is termed usually as a "block" CPE copolymer (bCPE). This type of CPE was employed by Paul et al. [2][3] who analyzed the effect of chlorine content on the mechanical properties of PVC/PE blends. Instead of block CPE copolymers, random CPEs (rCPE), obtained from PE in solution, have been also employed [4-6].

In the present paper we investigate on the compatibilising effect of an ethylene- vinyl chloride copolymer of similar chlorine content (40%) as the aforementioned CPEs, but obtained from reductive dechlorination of commercial PVC.

Experimental part

The materials used in this study were poly(vinyl chloride), PVC Etinox 650 (M_w=8.3 10^4, M_w/M_n=2.39), supplied by Aiscondel (Spain), a high-density polyethylene PE-

6006-L (M_w=1.7 10^5. M_w/M_n=7.70), supplied by Repsol-YPF., (Spain) and two copolymers of ethylene and vinyl chloride with 40% Cl content: a reduced PVC, RPVC, and, for comparison purposes, a randomly chlorinated polyethylene, rCPE, supplied by Aldrich. The reduction was performed by reductive dechlorination of the PVC sample (Etinox-650) with Lithium aluminium hydride ($LiAlH_4$). It is a stereospecific reaction in which chlorine atoms of isotactic and heterotactic triads are randomly replaced by hydrogen atoms, leaving sydiotactic triads virtually unaffected. [7]. Spectroscopic analysis of the samples by ^{13}C-RMN was performed with a Bruker 300MHz at 90°C, using a mixture of deuterated benzene and trichlorobenzene as a solvent. The analysis confirms that chlorine content is 37% for both RPVC and rCPE samples. The detected triad structure ratios, referring E to -CH2CH2- and V to -CH2CHCl-, are the following: RPVC (EEE 0.45; VEE 0.21; VEV 0.13; EVE 0.21) and rCPE (EEE 0.44; VEE 0.30; VEV 0.04; EVE 0.18; VVE 0.04).

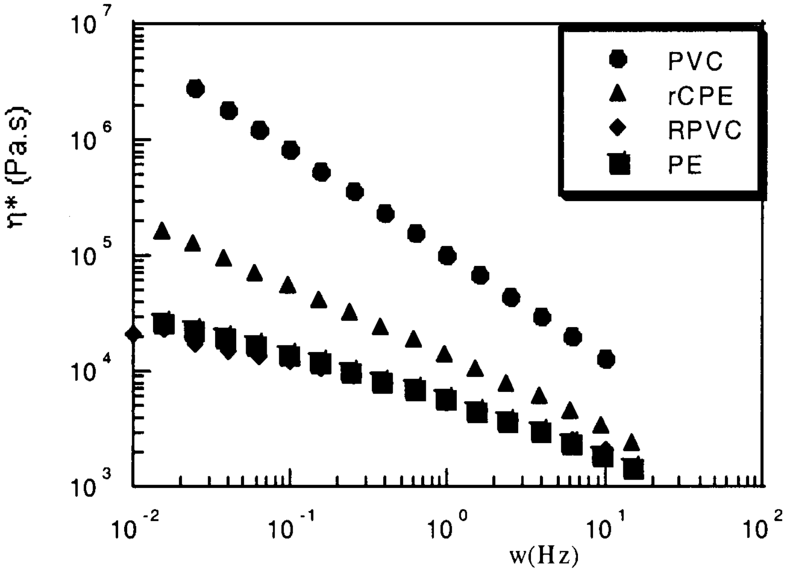


Figure 1 Complex viscosity as a function of angular frequency

Figure 1 shows a rheological characterization of the polymers, in terms of the complex viscosity as a function of frequency. It is seen that the viscosity of PVC is considerably higher than that of both PE and RPVC, whereas the viscosity of rCPE compatibilizer lies in between. Storage and loss moduli (not shown) reflect the similitude between PVC and rCPE, since in both polymers elastic behaviour prevails over viscous behaviour (G'>G''). However RPVC is more alike PE, as both polymers display a most typical polymer melt result, characterized by G''>G' in the terminal zone.

PVC/PE with a proportion in weight 50/50 has been used as the basic blend in this study. As compatibiliser or third component, rCPE and RPVC have been used. Ternary blends PE/PVC/rCPE and PE/PVC/RPVC with the composition 50/50/10, in weight, have been prepared.

All the blends have been premixed in the form of powder and, then, milled in a counter-rotating Guix-207 Two Roll Mill at 170°C for 4 min. Pure materials have been treated in the same way as the blends, in order to have the same thermomechanical history.

The morphology of the blends was analyzed using a Scanning Electron Microscopy (SEM) Hitachi S-2100 with an accelerating voltage of 15 Kv. The samples were cryogenically fractured under liquid nitrogen and then sputtered with a gold in vacuum. The morphology of the sheets obtained directly from the two-roll mill and of the filaments obtained in extrusion rheometry was observed.

Dynamic viscoelastic measurements of the melt were performed in a Rheometric ARES viscoelastometer, using parallel plate geometry at a temperature of 160ºC. Dynamic mechanical properties in the solid state were measured in a Polymer Laboratories Mark I Dynamic Mechanical Thermal Analyzer DMTA. Scans of temperature from –150 to 150ºC at a frequency of 1 Hz and a heating rate of 4ºC/min. were carried out in bending mode with samples of dimensions 10x5 mm and width of 1-2 mm. Extrusion rheometry measurements were carried out in a capillary rheometer Göttfert Rheograph 2002 using a capillary tungsten die of 1 mm diameter and length to diameter ratio (L/D) of 30. Tensile tests were carried out using an Instron 4301 at cross-speed of 10 mm/min and at room temperature and 50% humidity. Test specimens were cylindrical filaments of approximately 10 cm length and 1 mm width, which were prepared by extrusion in the capillary rheometer. The mechanical properties were determined from the load-elongation curve. Shrinkage measurements were performed using the aforementioned kind of filaments with average values of L_0=10 cm and R_0=1 mm.. The filaments were placed in a silicone oil bath at a temperature of T=180ºC and allowed to shrink: the length of the filament, L(t), was measured optically at various times up to 1200 s. No degradation was observed.

Results and Discussion

It is well known that PVC and PE are inmiscible polymers [5], which show a clear phase separation when they are mixed. Dynamic Mechanical results reported in the literature [8] show well defined PE and PVC phases, which are characterized by their corresponding glass transition temperatures. Our results of Figure 2, where tan δ spectra are presented, reveal that no alteration of PVC and PE respective α relaxation takes place when both polymers are mixed. These symptom of phase separation do not change when compatibilisers, RPVC or rCPE, are added to the binary PVC/PE blend: the relaxation peaks, associated to the respective glass transition temperatures remain in the same position. From this point of view no compatibilising effect can be attributed to these copolymers. However some minor, but significant, effects of the presence of a third component are detected. For instance the analysis of the spectra in the range –80 to –10ºC (Figure 2, inlet) reveals an increase of damping beyond to would correspond to simply additive rule. Furthermore, in ternary PVC/PE/RPVC and PVC/PE/rCPE systems we notice an increase of tanδ with respect to binary blend. This enhancement of damping is more noticeable when rCPE is used as the third component. The dual nature of rCPE and RPVC copolymers, with a certain affinity with both, PE and PVC, allow them to reach the interphase and interact with each of the pure polymers. Within this framework the increase of damping can be associated to new processes of molecular relaxation, due to a new phase with an onset of chain mobility different from both of the homopolyer domains. Since more damping is observed for PVC/PE/rCPE system, we can assume that rCPE is more efficient in order to modify PVC-PE interphase, than RPVC.

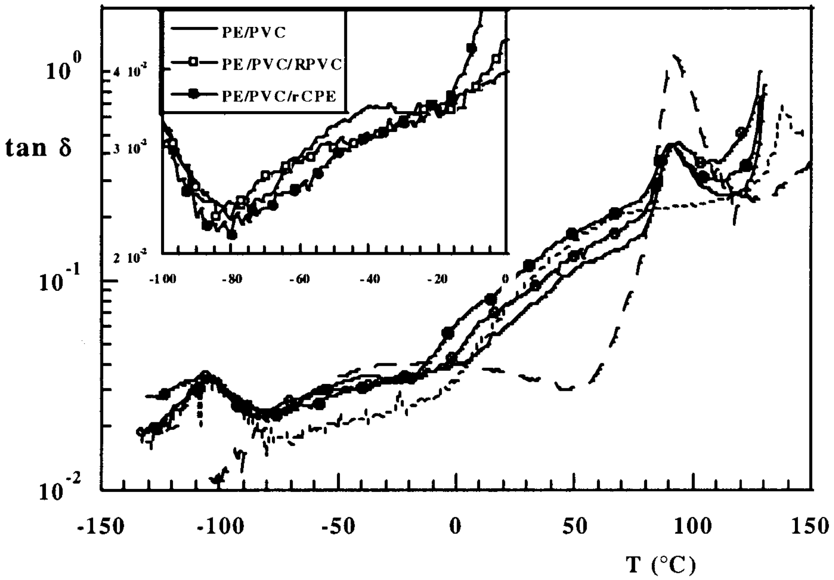
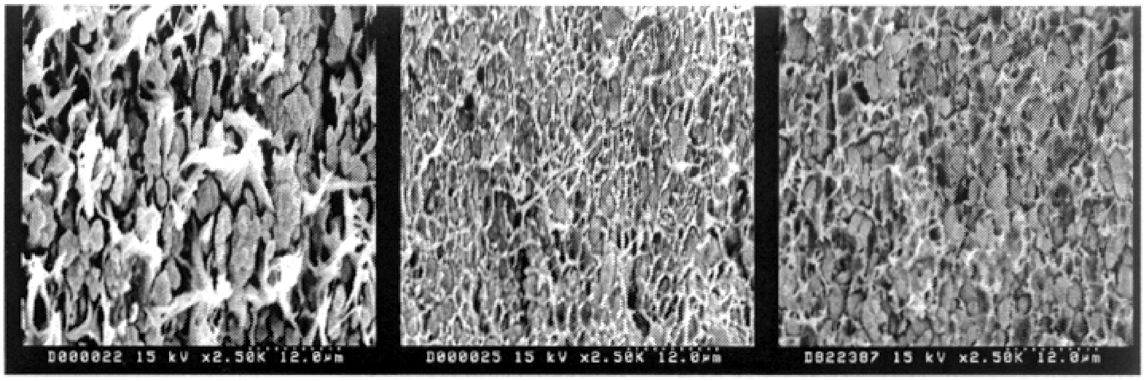


Figure 2 Dynamic mechanical spectra, loss tangent as a function of temperature of pure polymers(.......PE) (-----PVC) and its binary and ternary blends. In the inlet, the larger values of tanδ in the range (-80;-10) correspond to PE/PVC and the smaller to PE/PVC/rCPE.

The beta relaxation of PVC, which takes place at –50°C and it is connected with the start of the local-mode motion of the main chain, is also affected by the presence of a compatibiliser. The inlet of Figure 2 shows that beta relaxation is significantly reduced when RPVC or rCPE is added to the binary blend. This result reflects that the local mobility of PVC is altered by the presence of whatever of these copolymers, although we remark that the effect is more severe for rCPE. A similar result, that is to say considerable reduction of beta relaxation of PVC, has been reported by Shucai [8] when butadiene-acrylonitrile is mixed with PVC to improve impact properties.

Microscopic analysis reflects the aforementioned phase separation and gives insight on the effect of compatibilisers on the morphology of the binary blend. Figure 3 shows that in PVC /PE blends, PVC particles are able to constitute a network in a co-continous phase. The effect of this network in the viscoelastic properties of non-compatibilised and compatibilised PVC/PE molten blends has been analysed in a previous work [6]. This association between PVC particles is practically eliminated when rCPE is incorporated to the binary blend, since the compatibiliser acts favoring dispersion and reducing the size of particles. Once again we have to say that the effect of adding RPVC is similar, although attenuated, as far as PVC particles are not so small as in the case of adding rCPE.

Flow curves of the blends and original PE, obtained in a capillary rheometer, are shown in Figure 4. Pure polyethylene gives rise to smooth extrudates at low and moderate shear rates, but at 400s^{-1} slip-stick instability takes place. After slip-stick region, smooth extrudates are obtained again, but at 3000s^{-1} gross melt fracture is



a) b) c)

Figure 3 SEM microphotographs of the sheets obtained directly from the two-roll mill a)PE/PVC b)PE/PVC/rCPE c)PE/PVC/RPVC

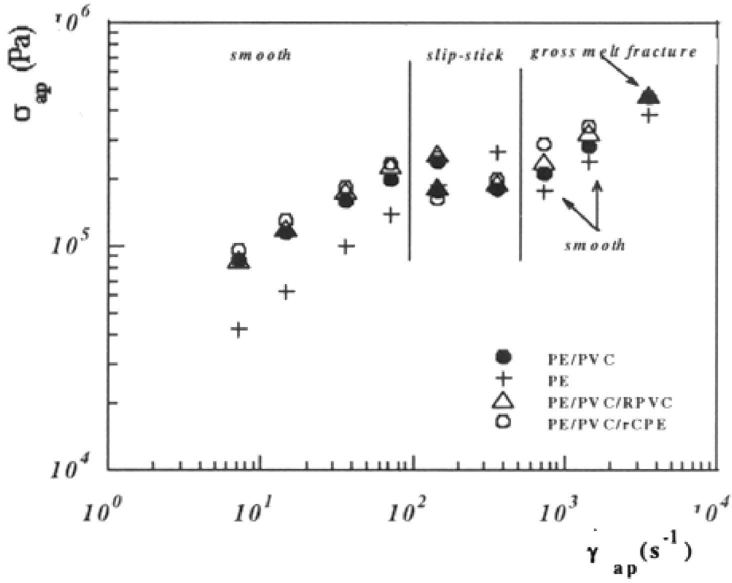
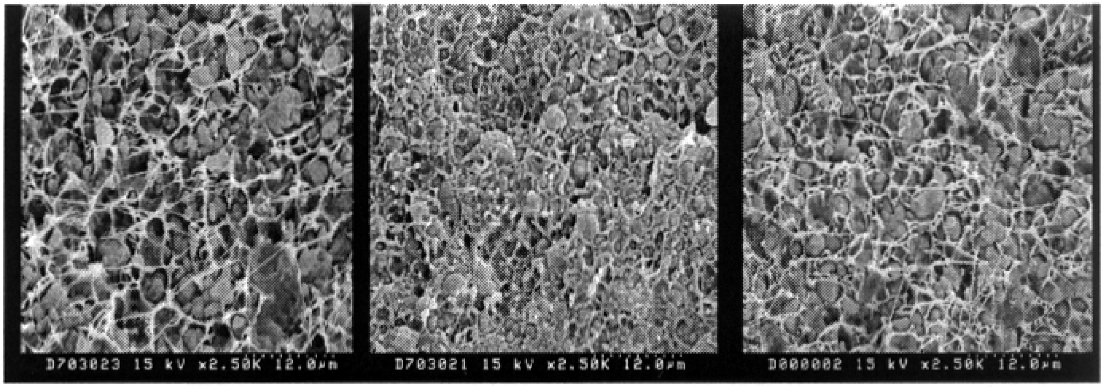


Figure 4 Flow curves of the blends and original PE obtained in a capillary rheometer at 190ºC

observed. Blends give rise to considerably higher shear stresses, associated to the particulate nature of PVC at 190ºC, which produces a suspension-like behavior. Slip-stick phenomenon takes place at 180 s^{-1}, a lower value than for pure PE, and, on the other hand, we remark that gross melt fracture disappears in the case of blends. The role played here by PVC, is that of a filler [9], that is to say suppression of an instability (melt fracture) associated to melt elasticity. The viscosity of ternary systems, specially the viscosity of PVC/PE/rCPE, increases with respect to binary blends. This is better noted at high shear rates, after slip-stick region. The viscosity enhancement observed in ternary systems, is a logical consequence of the improvement of the interaction between the matrix and PVC particles and the decrease of particle size. These factors imply a reduction of interlayer slip and an increase in effective volume. Our results coincide with those reported by Francis and George [10] for a HDPE/PVC blend modified with CPE. The SEM analysis of the cross section of the extrudates, presented in Figure 5, discloses a morphology which has been altered with respect to that observed in the samples prepared by compression.



a) b) c)

Figure 5 SEM microphotographs of the cross section of the extrudates a) PE/ PVC b) PE/PVC/rCPE c) PE/PVC/RPVC

We can observe a better dispersion of PVC particles in binary blends (compare Figures 3a and 5a), which is a consequence of the elongational and shear flows undergone by the blends during capillary extrusion. Much better dispersion and an increase of phase interaction is noticed when rCPE is added to the blend (Figure5b), a result which is compatible with the aforementioned viscosity enhancement. The compatibilising role of RPVC is not such a remarkable, since, even though dispersion is improved, the observed morphology (Figure 5c) is rather similar to that of binary blends.

The morphology developed during capillary extrusion rheometry is reflected in dimensional instability, as well as tensile mechanical properties. The former reflects the capacity of the system to recover residual stresses, like those produced by elongational flows at the entrance of the capillary. The extrudate shrinks and the recovery is analyzed using the Hencky measure of strain [11]:

$$\xi_r = \ln \frac{L_0}{L(t)} \qquad (1)$$

Where Lo is the original length of the extrudate and L(t) is the length at time t . Our experimental results are presented in Figure 6. The inlet of the figure shows the enormous recovery experienced by pure PE with respect to pure PVC. On the other hand, binary blend gives rise to a recovery which is considerably smaller to that corresponding to a single additive rule. As we reported in a previous paper [6], PVC micro-granulates act locking or anchoring the stress recovery of PE matrix. However, in the case of PVC/PE/rCPE ternary blends, we observe that this anchoring effect is considerably reduced, as recovery clearly increases with respect to binary blend. This result is related to the discussion regarding Figure 5: better dispersion of PVC micro-granulates and improved interaction between polymers, observed for ternary blend (compare Figure 5b to Figure 5a), makes anchoring effect of PVC less effective, allowing a larger recovery of PE matrix. In what the incorporation of RPVC concerns, we note only a slight increase of the recovery of PVC/PE/RPVC system with respect to binary blend. PVC particles still maintain at a large extent their capacity to lock PE recovery, despite the presence of RPVC. This is a logical consequence of the morphology disclosed in Figure 5, which shows a reduced capacity of RPVC to compatibilise the PVC/PE blend, at least compared to rCPE. (see Figures 5b and 5c)

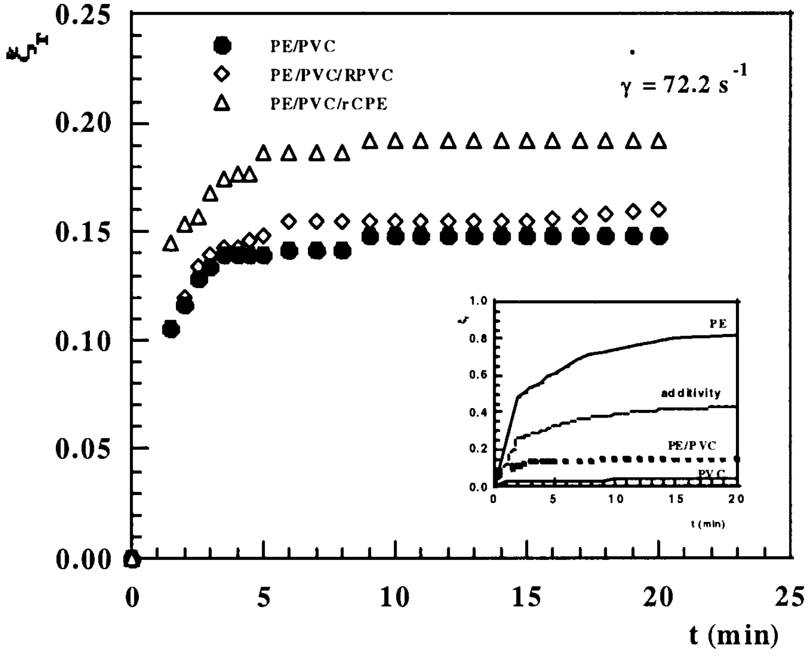


Figure 6 Hencky strains obtained in shrinkage measurements at 180ºC

Besides of CPEs, other copolymers have been used to improve the mechanical properties of binary PVC/PE blend, like polyethylene–methyl metacrylate graft copolymer [12], poly((butadiene –block-acrylonitrile)-block-butadiene) [13] and ethylene-propylene rubber [14].A general conclusion of the reported results is that an improvement of the ductility can be considered as a symptom of a compatibilising effect of the additive incorporated to the blend. Ductility increase is a consequence of the role played by the compatibiliser: reduction of the interfacial tension which leads to a diminish of the size of the domains and to an increase of the adhesion between phases.

To the difference with reported literature results, which have been determined with moulded samples, our tensile experiments data were obtained using fibers (extrudates). Therefore the values of the elongation at break, which are determined from data of Figure 7, are considerably lower than those reported in the literature [2,10,15-16]. However the increase in ductility when rCPE is added to the binary blend is evident: elongation at break increases from 2% (+ - 0.1%) for PE/PVC to 10% (+-0.5%) for PE/PVC/rCPE. In Figure 7 we also include the results obtained when block polyethylene chloride, bCPE, is used as compatiliser, which are very alike to those of rCPE. Actually, as we have shown in previous works; [6], the compatilising effect of both, rCPE and bCPE, are very similar, in what aspects like morphology, mechanical properties and rheology concern. Nevertheless, the effect of the addition of RPVC is less patent, since elongation to break increases only up to 5.5% (+-0.5%) for PE/PVC/RPVC ternary system. This result reflects the inferior capacity of the

RPVC to act as a compatibiliser, in comparison with CPEs. Tensile stress-strain curves of Figure 7 show, on the other hand, an enhancement of the tensile strength for PE/PVC/RPVC blend. This is an interesting result from a practical point of view, since polymer industry would welcome a material based on PE/PVC blends with an enhanced tensile strength.

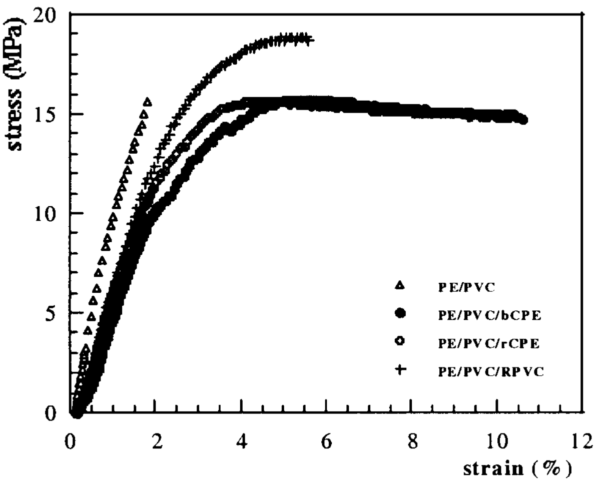


Figure 7 Stress-strain curves obtained with filaments.

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References

1. Schramm JN, Blanchard RR,(1970) The use of CPE as a compatibilizer for of waste plastis materials. In: Palisades Section SPE RETEC, Cherry Hall, New Yersey.
2.. Paul DR, Locke CE, Vinson CE (1973) Polym Eng Sci. 13:202.
3. Locke CE, Paul DR (1973) Polym Eng Sci 13: 308
4. Zarraga A (2001) PhD thesis, University of the Basque Country, UPV/EHU San Sebastián Spain.
5. Paul DR (1978) Interfacial agents(Compatibilizers) for polymer bleds.In: Paul DR,Newman S (ed)Academic Press Inc, New York vol 2.
6. Zarraga A, Muñoz ME, Peña JJ, Santamaría A, Polym Eng Sci, accepted for publication.
7. López D, Dahmani M, Mijangos C, Brûlet A, Guenet JM. (1994) 27: 7415
8. Shucai (1994) Intern J Polymeric Matter 27:21
9. Han CD (1981) Multiphase flow in polymer processing. Academic Press, New York.
10. Francis J, Georges KE (1991) Natl Conf Adv Polym Technol 203
11. Laun HM, Münstedt H (1978) Rheol Acta 17: 415.
12. Boutevin B., Pietrasanta Y., Taha M., Sarraf T. (1985) Polym. Bull. 14:25
13. Kroeze E, Brinke GT, Hadziioannou G (1997) Polymer 38:379.
14. Ha C,Park H, Cho W (2000) J Appl Polym Sci 76:1048
15. Francis J, George KE (1992) J.Elastom.Plast. 24:151
16. He P, Huang H, Xiao W,Huang S Cheng S.(1997) J. Appl Polym Sci 64:2535