

ESTIMATION OF THERMODYNAMIC AND KINETIC SECONDARY NUCLEATION PARAMETERS IN POLY(STYRENE-CO-MALEIC ANHYDRIDE)/POLY(ϵ -CAPROLACTONE) BLENDS

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Abstract

The estimated equilibrium melting points of the poly(ϵ -caprolactone) (PCL) fraction in poly(styrene-co-maleic anhydride)/poly(ϵ -caprolactone) blends (PSMA14/PCL), where the PSMA has 14 mol% of maleic anhydride units, were successfully analyzed by means of the Nishi-Wang equation yielding a negative Flory-Huggins interaction parameter ($\chi = -1.46$). This result indicates strong interactions between the blend components, whose magnitude do not change with composition. The kinetics of the PCL spherulitic growth was investigated as a function of composition and crystallization temperature by polarized optical microscopy and analyzed using the traditional Lauritzen-Hoffman (*LH*) secondary nucleation theory, as well as a modified version of it. The composition dependence of nucleation constants, K_g , in crystal growth regime II suggests that crystal fold energy, σ_e , decreases with the addition of PSMA14, but when the concentration of PSMA14 reaches 20% or more, non additional effect is observed, a fact that was attributed to the PCL effective concentration considered in the Lodge and McLeisch model for miscible blends.

Keywords: Miscible Blends, Crystallization, Poli(ϵ -caprolactone).

Resumen

Mediante la ecuación de Nishi-Wang se llevó a cabo en este trabajo un análisis de los puntos de fusión en equilibrio estimados de la fracción de poli(ϵ -caprolactona) (PCL) contenida en mezclas de poli(estireno-co-anhídrido maleico)/poli(ϵ -caprolactona) (PSMA14/PCL), donde el PSMA posee 14% molar de unidades de anhídrido maleico. Como resultado se obtuvo un parámetro de interacción de Flory-Huggins negativo ($\chi = -1.46$), resultado que indica la existencia de fuertes interacciones entre los componentes de la mezcla, cuya magnitud no cambia con la composición. La técnica de microscopía óptica de luz polarizada permitió estudiar la cinética de crecimiento esferulítico de la PCL en función de la composición y de la temperatura de cristalización. Posteriormente, se aplicó la tradicional teoría de nucleación secundaria de Lauritzen-Hoffman (*LH*), así como también una de sus versiones modificadas. La dependencia de las constantes de nucleación, K_g , con la composición en el régimen de crecimiento II sugiere que la energía de pliegue disminuye con la adición de PSMA14. Sin embargo, cuando la concentración de PSMA14 alcanza el 20% o más, no se observa efecto adicional, hecho que se atribuyó a la concentración efectiva de PCL que se considera en el modelo de Lodge y McLeisch para mezclas miscibles.

Palabras Claves: Mezclas miscibles, Cristalización, Poli(ϵ -caprolactona).

1. INTRODUCCION

Polymer blending has been often selected as a way to obtain new polymers for technological applications, essentially due to economic reasons. Although most of the polymer blends systems have shown to be immiscible, blending with polycaprolactone has proven to be very useful for preparing miscible blends. Recently, we reported a detailed study on the molecular dynamics and crystallization kinetics in poly(styrene-co-maleic anhydride)/poly(ϵ -caprolactone) PSMA14/PCL

blends [1], where the intimate mixing of the components at a molecular level was demonstrated through the observation of PSMA14 interlamellar insertion, a significant increase in the half-crystallization time, a hindering of the pre-cooperative PCL motions assigned to the β relaxation, and the study of the compositional variation of the glass transition. The higher equilibrium melting point depression detected for PSMA14/PCL blends compared to that obtained for blends of PCL with PVC [2], Phenoxi [3] and

SAN19.5 [4] suggested a lower Flory-Huggins interaction parameter that was not estimated in such publication, where even the possibility of a composition dependent parameter was discussed.

The properties of blends comprising semicrystalline components depend strongly on the miscibility and, therefore, on the crystallinity and crystalline morphology. The crystallization behavior of polymeric materials has been typically studied through both isothermal and non-isothermal crystallization measurements. During the isothermal crystallization of the crystallizable component in a miscible blend with an amorphous polymer three types of segregation have been identified [5]: interlamellar [2,3,6], interfibrillar [2,3,7], or interspherulitic [3,7,8]. In PSMA/PCL blends, the occurrence of interlamellar segregation has been demonstrated [1,9]. The liquid-solid phase segregation that takes places during crystallization requires the diffusion and segregation of the amorphous component from the crystallizing growth front; among the parameters that affect this process, the rigidity of the amorphous component and the Flory-Huggins interaction parameter may be mentioned. Previous studies on PCL blends have shown that the application of the Nishi-Wang treatment [10] accurately allows the determination of such parameter and, depending on the linearity of the data, a composition dependent parameter may be identified [11-13]. In addition, the dilution of a crystallizable component due to the addition of an amorphous polymer may affect the formation of secondary nuclei and the chain transport process to the crystal growth front. A detailed study of these effects may be performed by applying the Lauritzen-Hoffman (*LH*) theory [14], from which the variation of parameters such as the surface free energy and the fold free energy may be investigated. Up to our knowledge, only one report about PSMA/blends may be found in the literature, in which an analysis of the growth rate is carried out as a function of the amorphous component content, but only in blends containing less than 20%; nevertheless, the different thermodynamic and kinetic parameters were not determined. It was, therefore, aim of this work to study the variation of such parameters in the PCL crystallization upon addition of PSMA.

2. EXPERIMENTAL SECTION

2.1 Preparation of the Blends

For the preparation of the blends, a poly(ϵ -

caprolactone) (PCL Tone-787), manufactured by Union Carbide ($M_n = 73$ kg/mol, $M_w = 112$ Kg/mol) and a poly(styrene-*co*-maleic anhydride) (PSMA14) purchased from Aldrich Chemical Co, Inc. ($M_n = 100$ kg/mol, $M_w = 174$ kg/mol) were used. The PSMA14 copolymer contained 14 mol% of maleic anhydride (MA) units randomly distributed through the chain. PSMA14/PCL blends were prepared in a laboratory scale screw extruder at temperatures that were set at 180°C-235°C in the die and in the barrel zone, depending on blend composition (0/100, 10/90, 30/70, 40/60, 70/30, 90/10, 100/0), processing them twice to ensure their homogeneity as was previously demonstrated [1,9]. It should be remarked that under such conditions and the low residence time in the extruder no degradation of the components was observed [1,9].

2.2 Characterization of the blends

Compression molded sheets were prepared from neat PCL, PSMA14, and blends at temperatures varying from 170°C to 195°C, depending on composition; then, the sheets were quenched in cold water.

For Differential Scanning Calorimetry (DSC), small disc samples were cut (13.0 ± 0.1 mg) from the compression molded sheets and encapsulated in aluminum pans. A Perkin-Elmer DSC-7 was used to study the thermal behavior of all compositions under ultra high purity nitrogen atmosphere. Standard cooling and heating DSC scans were performed at 10°C/min after they were held in the melt at 170°C for 5 minutes. Isothermal crystallizations were performed after the samples were heated to 170°C and annealed at that temperature for 5 min. Then, they were quenched at a rate of 80°C/min to a selected crystallization temperature, T_c , where they were held for a crystallization time, t_c , equal to three times the crystallization time deduced from the isothermal exothermic peak. Finally, a heating scan from T_c to 170°C was recorded at 10°C/min.

A Zeiss Polarizing Optical Microscope coupled with a hot-stage was used to investigate the superstructure formation in isothermally crystallized samples that were previously cut in a microtome. These sections were held for 5 min at 170°C and quenched down to a selected crystallization temperature, T_c , under polarized light, to follow the spherulitic growth.

3. RESULTS AND DISCUSSION

In previous works we reported miscibility between PSMA14 and PCL and demonstrated that the Fox equation accurately predicts the experimental results of the bulk glass transitions [1,9]. Consequently, the crystallization behavior was significantly affected in comparison with neat PCL and those blends containing 35% and 40% PSMA14, so that the system could hardly crystallize upon cooling and exhibited cold-crystallization upon heating as may be appreciated in Figure 1a, where some examples are presented.

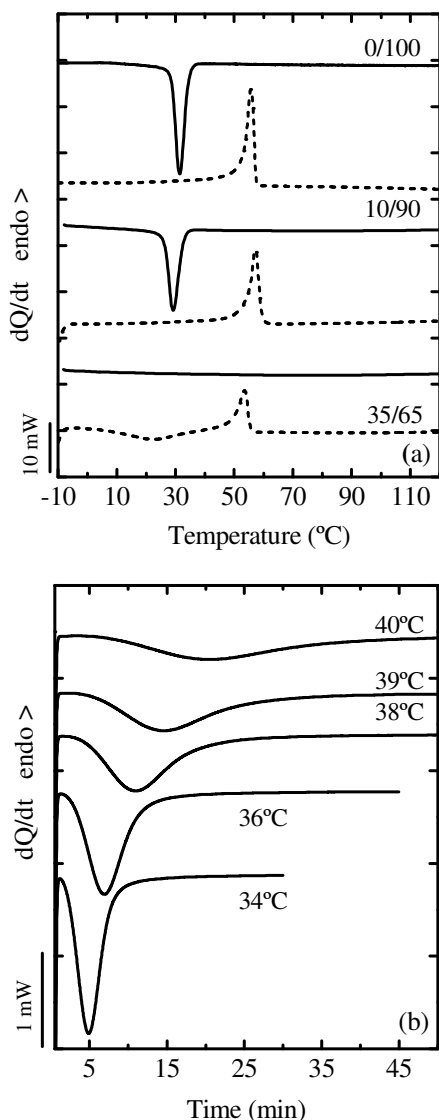


Figure 1. DSC cooling and heating scans (10°C/min) of PSMA14/PCL blends. (b) DSC isothermal crystallizations of PSMA14/PCL 35/65.

Even though no crystallization was observed upon cooling for blends with 35% and 40% PSMA14, we

could calculate in a previous study [9] the equilibrium melting points, T_m^0 , by performing isothermal crystallizations, from which very well defined exotherms could be observed as it is shown in Figure 1b for PSMA14/PCL 35/65.

As expected, as the crystallization temperature increases, the crystallization exotherms appear at higher crystallization times and the peaks become wider, indicating the typical nucleation problems associated to the high mobility of the chains at high temperature, which results in problems for primary nuclei activation and secondary nucleation. From T_m^0 calculations it was evident a marked depression of this value for the PCL fraction with the PSMA14 content [1], being this depression much more stronger in comparison with other PCL blend systems containing poly(vinyl chloride) (PVC), poly(styrene-*co*-acrylonitrile) (SAN19.5) with 19.5% acrylonitrile, or poly(hydroxyether of bisphenol A) (Phenoxy) as may be observed in Figure 2.

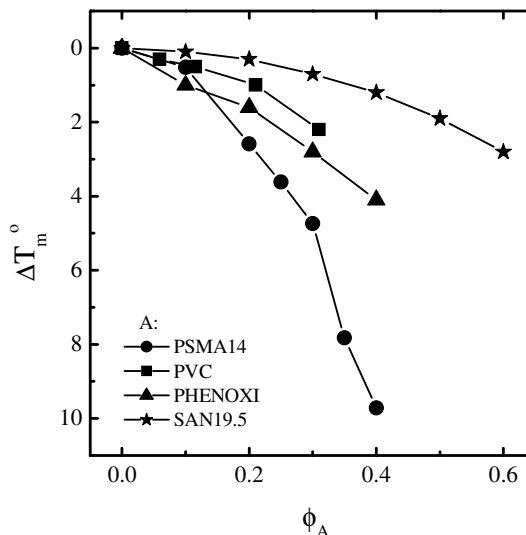


Figure 2. Equilibrium melting-point depression of the PCL fraction in blends A/PCL as a function of the amorphous polymer A content [1].

Due to the fact that the variations of the equilibrium melting points, T_m^0 , are related to the Flory-Huggins interaction parameter, χ_{AB} , we calculated in this work this parameter using the Nishi-Wang treatment [10]. The method involves a comparison of the equilibrium melting point of a neat semicrystalline polymer to that of the same polymer in blends of different compositions. For a binary mixture of two relatively high molecular weight polymers, one semicrystalline and one non-crystalline, Nishi and

Wang showed that [10]:

$$\frac{1}{T_{mb}^0} - \frac{1}{T_m^0} = -\frac{RV_{Bu}}{\Delta H_f^0 V_{Au}} \chi_{AB} \phi_A^2 \quad (1)$$

where T_m^0 and T_{mb}^0 are, respectively, the equilibrium melting points of the neat semicrystalline component and of the blend containing a volume fraction of amorphous component ϕ_A . R is the universal gas constant, ΔH_f^0 is the molar heat of fusion for PCL, V_{Au} and V_{Bu} , are the molar volumes of the amorphous and crystalline units, respectively [15]. Thus, a plot of $(1/T_{mb}^0) - (1/T_m^0)$ vs. ϕ_A^2 should yield a straight line with a slope proportional to χ_{AB} and a zero y-intercept. Figure 3 shows the Nishi-Wang plot for the semicrystalline PSMA14/PCL blends; from the slope of the linear fit, a value of $\chi_{AB} = -1.46$ was determined with a $R^2 = 0.995$. The linearity of the curve indicates that the interaction parameter is not composition dependent [11-13]. It should be remarked that the value of -1.46 represents one of the lowest values reported for blend systems containing PCL; thus, for SAN19.5/PCL [4], *p*-CIPS/PCL [15] and PBS/PCL [16] blends, for example, values of -0.0051 , -0.66 , and -0.11 have been reported. Such low χ_{AB} for the PSMA14/PCL system are indicative of strong interactions between both components, in agreement with previous morphological observations [1,9].

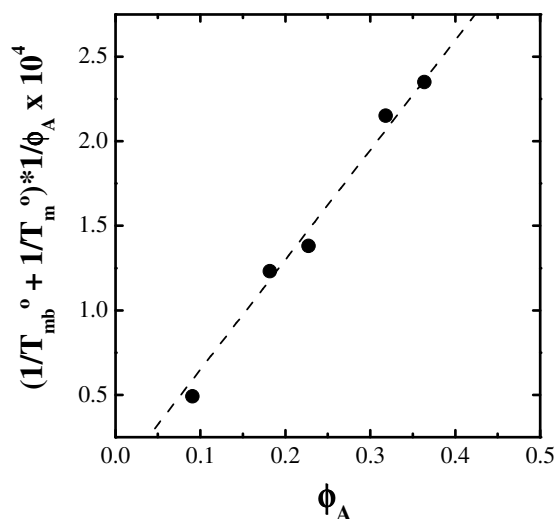


Figure 3. Nishi-Wang plot for semicrystalline PSMA14/PCL blends.

When miscible blends are considered, it is interesting to investigate how certain PCL parameters are affected by the presence of PSMA14. Isothermal crystallization kinetics data may be analyzed using a variety of models; between these

models the following may be mentioned: a) the Lauritzen and Hoffman (*LH*) model, which provides analytical expressions for the growth rate as a function of the supercooling [14, 17-20], b) the Sadler and Gilmer (*SG*) theory, which considers the thermal roughening phenomenon observed in low molecular weight molecules [17-20], c) the Strobl treatment that argues that a mesomorphic precursor phase is formed before the most stable phase appears [21,22], and d) the extensive computer simulations performed by Muthukumar [23-24]. Even though the model of nucleation and growth proposed by Lauritzen and Hoffman (*LH* treatment) has been under much criticism lately, it is still one of the few treatments that provides easy to use mathematical expressions that are capable of describing well the experimental data and therefore it continues being widely employed [25-27]. Thus, in a first approximation, we applied, as will be shown in the next section, the Lauritzen and Hoffman (*LH*) treatment [14] to neat PCL as well as to the PCL fraction contained in the blends. In order to accomplish this, the kinetics of the PCL spherulitic growth was followed. In semicrystalline miscible blends, the crystallization range changes due to the presence of the non crystallizable component since glass transitions, T_g , and melting points, T_m , are composition-dependent. PSMA14/PCL blends exhibit, as have been previously reported [1,9] a melting point depression and a T_g increase when the amorphous component content is increased; therefore, the crystallization window is reduced. Within this narrow crystallization window, we have previously shown that these homogeneous blends crystallize forming ring-banded spherulites (see Figure 4) whose ring periodicity showed a dependence on composition and crystallization temperature [1].

From the polarized optical micrographs a linear growth of the spherulitic radius with time was observed, indicating that the composition of the molten phase remains constant at the growth front because the PSMA is trapped in the interlamellar region as has been observed by transmission electron microscopy; under these conditions, the PCL retains its orthorhombic structure [1]. It is known that segregation of the non-crystallizable component may be interlamellar, interfibrillar or interspherulitic; PSMA14 trapping in the interlamellar regions indicate that the favorable interactions between the PSMA14 diluent molecules and the amorphous portions of the crystallizable

component (expressed in a low Flory-Huggins interaction parameter) dominates over the entropic driving force that tends to pull the diluent molecules out of the interlamellar regions and the tendency of the progressive crystallization to remove these molecules of the non-crystallizable component out of these areas [28].

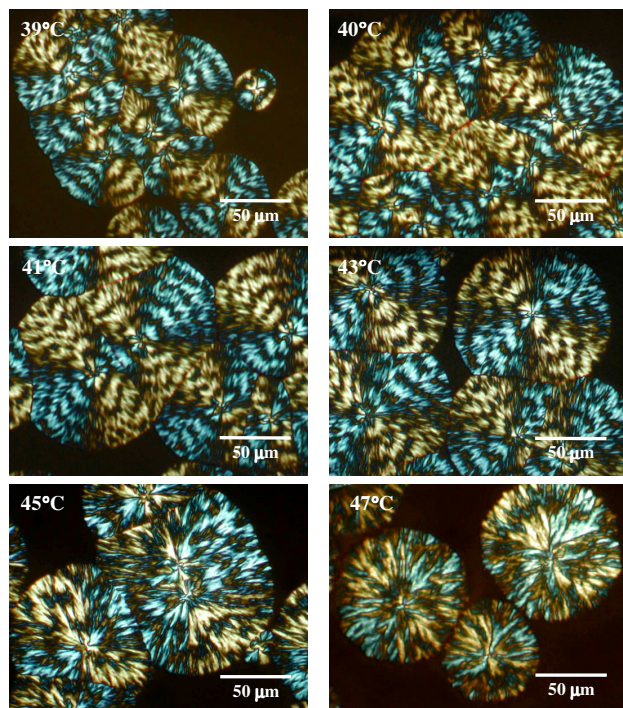


Figure 4. POM images obtained during isothermal crystallization of PSMA14/PCL 30/70 at different crystallization temperatures.

Figure 5a shows the variation of PCL spherulites growth rate, G , obtained from the slope of the radius vs. time curves for each composition at selected crystallization temperatures. As usual for many polymer systems, only the increase of G by reducing T_c is observed due to the favorable thermodynamic force for the nucleation. The dependence of G with T_c is weaker at higher PSMA14 content (see Figure 5b), which is a consequence of the narrowing of the PCL crystallization window, a fact that reduces the diffusion ability of the PCL chains towards the growth front; besides this, it is known that the dilution of a crystallizable component affects the free energy for nucleation, both factors affecting G . In Figure 5a it may also be appreciated a more marked reduction of G at higher supercoolings. These results are in agreement with those reported by other authors that blended PCL with amorphous polymers [2-4,7,29]. Defieuw *et al.* [30] also reported the variation of G with composition, but only for

blends containing less than 20% PSMA because they could not follow the spherulitic growth in other compositions due to the high nuclei density.

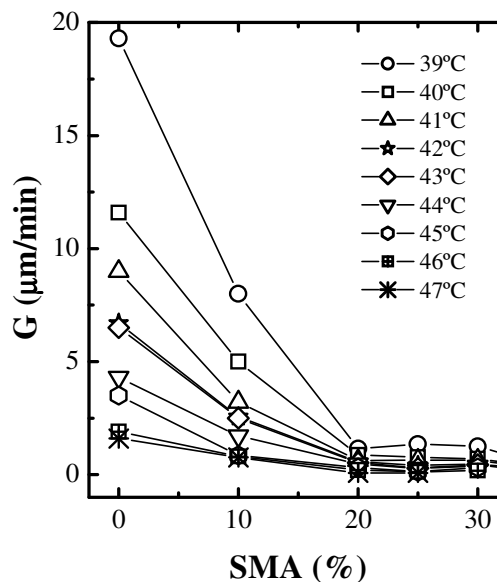
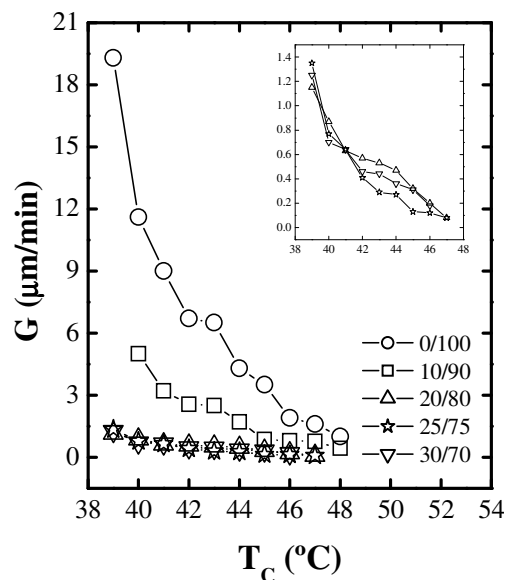


Figure 5. Isothermal spherulitic growth rate, G , as a function of (a) crystallization temperature, where the inset is a magnification of the low G values part of this figure, and (b) composition.

Once we obtained G , we used these values to study the global crystallization kinetics by applying the Lauritzen and Hoffman (LH) treatment in PCL-rich blends to investigate the diluent effect of PSMA14 on the transport term of equation (2), which is well known that dominates at high supercoolings. The temperature dependence of the spherulite growth rate, G , is given by [14,31]:

$$G = G_0 \exp\left(\frac{-U^*}{R(T_c - T_\infty)}\right) \exp\left(\frac{-K_g}{T_c \Delta T f}\right) \quad (2)$$

where the preexponential factor G_0 is a growth rate constant that is essentially temperature-independent, U^* is the activation energy for the transport of crystallizable segments to the crystal front, T_∞ is the temperature below which segmental motions cease, and it is usually taken as $T_g - 30\text{K}$, $\Delta T = T_m^0 - T_c$ is the supercooling where T_m^0 is the equilibrium melting point obtained for each composition [1]; T_g values were obtained from Fox equation [32]. f is a correction factor equal to: $2T_c/(T_c + T_m^0)$ and K_g is an important parameter related to the energetic barrier for secondary nucleation given by:

$$K_g = \frac{j b_0 \sigma \sigma_e T_m^0}{k \Delta h_f} \quad (3)$$

where b_0 is the thickness of a molecular layer, σ is the lateral surface energy, σ_e is the fold surface energy, k is the Boltzman constant and Δh_f the heat of fusion of a perfect crystal. The value of j is characteristic of the crystallization regime and changes from 4 in regime I at low undercooling to 2 in regime II at intermediate undercooling and back to 4 in regime III, at high undercooling.

Figure 6 shows *LH* plots for neat PCL and PSMA14/PCL blends. As can be seen, there is no observable change in the slope of each curve in the range of temperatures studied, indicating that no change of the crystallization regime is occurring. From the slope of the curves, the value of K_g was calculated. The values of $\sigma \sigma_e$ were obtained from eq. (3) assuming that the spherulites grow under Regime II; i.e., $j=2$. This assumption is based on the reports given by other authors for PCL for the crystallization temperature range investigated in this work [33-35]. Results extracted from Figure 6 are listed in Table 1.

Table 1. Parameters obtained from the experimental data after applying the *LH* treatment.

PSMA14/ PCL	G_0 (cm/s)	K_g (K^2)	$(\sigma \sigma_e)^{1/2}$ (erg/cm^2)	σ_e (erg/cm^2)	q (kcal/mol)
0/100	63.84	88714	26.5	99.9	5.4
10/90	5.49	62644	22.4	71.3	3.8
20/80	0.28	38716	17.7	44.7	2.4
25/75	0.43	38767	17.7	44.8	2.4
30/70	0.48	38816	17.7	44.7	2.4

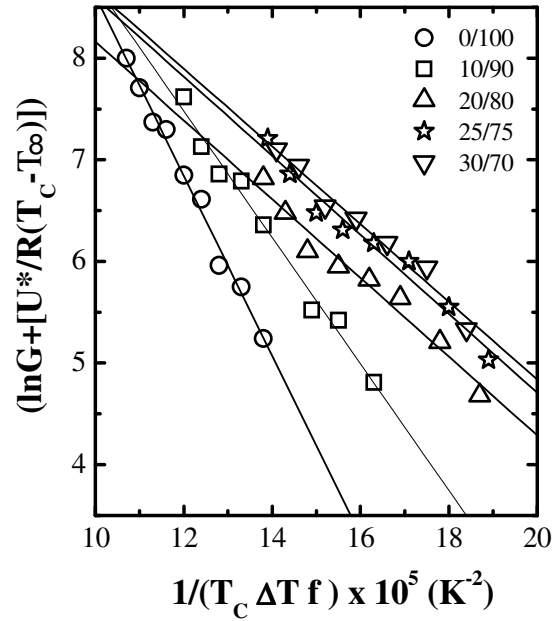


Figure 6. Lauritzen-Hoffman plots for the PCL fraction contained in PSMA14/PCL blends.

Neat PCL shows values that are in agreement with the findings of other authors; the fold surface energy, σ_e is only slightly higher than the value given by Phillips *et al.* [33,34] and slightly lower than the reported one by Goulet *et al.* [35]. From Table 1 it is evident a reduction of $(\sigma \sigma_e)^{1/2}$ upon PSMA14 addition, but once the blend has more than 10% PSMA14, $(\sigma \sigma_e)^{1/2}$ remains constant. From this product, the fold surface energy, σ_e , may be determined calculating the lateral surface free energy, σ , by means of the Thomas-Stavely relation [36]:

$$\sigma = 0.1 \Delta h_f \sqrt{a_0 b_0} \quad (4)$$

where a_0 and b_0 are the thickness and width of a chain segment, respectively. The value of σ was $7.03 \text{ erg}/\text{cm}^2$. In addition, the work done by the chain to form a fold, q , was obtained from:

$$q = 2 a_0 b_0 \sigma_e \quad (5)$$

The decrease of σ_e with the increase of concentration of non-crystallizable material has been reported for a series of polymer blends [37-39] when the amorphous component is located in interlamellar or interfibrillar regions. This decrease of the fold surface energy has been explained supposing that the presence of the amorphous component produces an increase of the folding entropy and bears to the formation of crystals with

more disordered folding surfaces [39]. It must be noted that in the examples reported in the literature, as well as in the PSMA14/PCL blend system, the melt viscosity increases with the amount of amorphous material. In Table 1 an initial decrease of σ_e may be observed, but then it remains constant. The non-variability of σ_e with blend composition from a specific composition may be explained based on our previous work [1] where we demonstrated, through thermally stimulated depolarization currents (TSDC), the existence of two effective glass transition temperatures, in agreement with the prediction of Lodge and McLeisch model for miscible A/B systems [40], which are attributed to concentration fluctuations originated by chain connectivity effects. These effects are, therefore, related to the intramolecular origin of the folding surface that have led to some authors to propose that σ_e should be independent of blend composition [39,41]; because it is assumed that the diluent molecules do not penetrate the fold-melt interfacial region. The detection of two effective glass transitions in our case is associated to the self-concentration; i.e., the average local composition perceived by each component blend, which may be quite different from that of the bulk. Thus, once the PSMA14 has been blended with PCL up to certain composition, it has little influence on the PCL fold surface energy probably because of the PCL effective concentration that is richer in PCL than the nominal blend concentration.

Based on the previous results, it would be then more appropriate to use the modified version of the *LH* treatment [42-44] for studying the crystallization kinetics of blends containing a crystallizable and a non-crystallizable polymer. Thus, more reliable parameters may be obtained. For these blends, the modified *LH* equation is the following:

$$\ln G - \ln \phi_2 + \frac{U^*}{R(T_c - T_\infty)} - \frac{0.2T_m^0 \ln \phi_2}{\Delta T} = \ln G_0 - \frac{K_g}{T_c \Delta T f} \quad (6)$$

where ϕ_2 is the volume fraction the crystallizable component.

Figure 7 presents the results obtained after applying equation (6). Compared with Figure 6, a vertical shift of the curves is observed together with a slight variation in the slope, but without no observable changes in the slopes in the temperature range

explored; again, a good linear fit is obtained. Table 2 lists the values extracted from Figure 7.

Table 2. Parameters obtained from the experimental data after applying the modified *LH* treatment.

PSMA14/ PCL	G_0 (cm/s)	K_g (K ²)	$(\sigma\sigma_e)^{1/2}$ (erg/cm ²)	σ_e (erg/cm ²)	q (kcal/mol)
0/100	63.84	88714	26.5	99.9	5.4
10/90	6.35	56882	21.3	64.8	3.5
20/80	0.35	30434	15.7	35.1	1.9
25/75	0.57	29025	15.4	33.5	1.8
30/70	0.67	27465	14.9	31.7	1.7

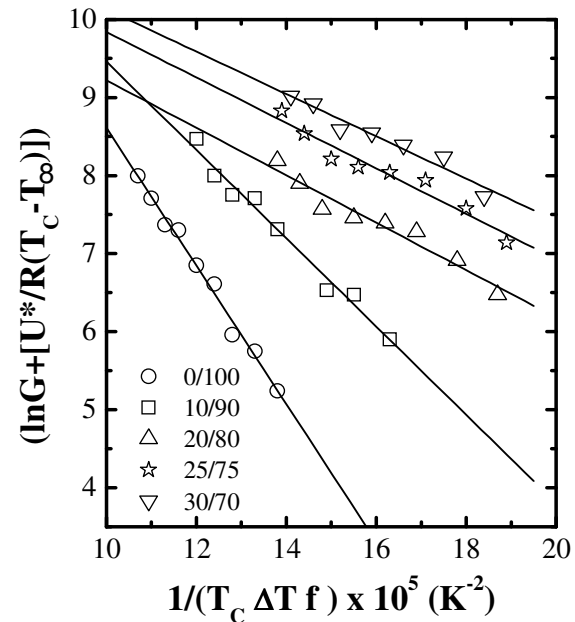


Figure 7. Modified Lauritzen-Hoffman plots for the PCL fraction contained in PSMA14/PCL blends.

In Table 2 it can be appreciated that, although slightly lower values are obtained in the blends, they exhibit a similar tendency to those presented in Table 1. An initial decrease of the energy and work to form a fold of about 65% is observed, evidencing again the formation of more stable surfaces due to favorable interactions between both components, but upon increasing the amount of PSMA14, no further significant decrease is obtained (only an additional decrease of 3%). This may be attributed, as explained above, to the PCL effective concentration that is richer in PCL than the nominal blend concentration.

4. CONCLUSIONES

The evaluation of the Flory-Huggins interaction

parameter, χ_{AB} , applying the Nishi-Wang approach for analyzing the equilibrium melting point depression yields a value of -1.46 , one of lowest values reported for polymer blend systems including PCL, which indicates the existence of stronger interactions between the blend components. Spherulitic growth data demonstrated that the crystallization is not a diffusion-controlled process and allowed us to use the Lauritzen-Hoffman kinetic theory of crystal growth to estimate the fold surface energy, σ_e , as a function of blend composition. The addition of PSMA14 to PCL has an initial effect of decreasing σ_e ; nevertheless, further increase of PSMA14 has not a significant effect on this parameter, a fact that was attributed to the PCL effective concentration.

5. ACKNOWLEDGMENTS

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6. REFERENCES

- [1] Balsamo V, Newman D, Gouveia L, Herrera L, Grimaú M, Laredo E. *Polymer* 2006; **47** (16): 5810-5820.
- [2] Eastmond GC. *Adv. Polym. Sci.* 1999; **149**: 59-223.
- [3] Defieuw G, Groeninckx G, Reynaers H. *Polymer* 1989; **30** (12): 2164-2169.
- [4] Kressler J, Kammer HW. *Polym. Bull.* 1988; **19** (3): 283-288.
- [5] Vanneste M, Groeninckx G, Reynaers H. *Polymer* 1997; **38** (17): 4407-4411.
- [6] Kammer HW, Kummerlowe C. En: *Advances in Polymer Blends and Alloys Technology*, Vol. 5, Lancaster (USA): Technomic Publishing Co. Inc., 1994, 132-160.
- [7] G. Defieuw, G. Groeninckx, H. Reynaers. *Polymer* 1989; **30** (4): 595-603.
- [8] Martuscelli E, Silvestre C, Addonozio ML, Ametino L. *Die Makromol. Chem.* 1986; **187** (6): 1557-1571.
- [9] Balsamo V, Gouveia L, Herrera L, Laredo E, Méndez B. *Rev. LatinAm. Metal. Mater.* 2004; **24** (1): 17-30.
- [10] Nishi T, Wang TT. *Macromolecules* 1975; **8** (6): 909-915.
- [11] Cheung YW, Stein RS. *Macromolecules* 1994; **27** (9): 2512-2519.
- [12] Balsamo V, Calzadilla N, Mora G, Müller AJ. *J. Polym. Sci. Polym. Phys.* 2001; **39** (7): 771-785.
- [13] Hernández MC, Laredo E, Bello A, Carrizales P, Marcano L, Balsamo V, Grimaú M, Müller AJ. *Macromolecules* 2002; **35** (19): 7301-7313.
- [14] Hoffman JD, Miller RL. *Macromolecules* 1988; **21** (10): 3038-3051.
- [15] Aroguz AZ, Engin HH, Baysal BM. *Eur. Polym. J.* 2007; **43** (2): 403-409.
- [16] Bikiaris DN, Papageorgiou GZ, Achilias DS, Pavlidou E, Stergiou A. *Eur. Polym. J.* 2007; **43** (6): 2491-2503.
- [17] Mandelkern L. En: *Crystallization of Polymers*. Vol. 2. Cambridge: Cambridge University Press, 2002. 101-121.
- [18] Mandelkern L. En: Mark JE (ed.) *Physical Properties of Polymers*. Cambridge: Cambridge University Press, 2004. 245-266.
- [19] Shultz JM. *Polymer Crystallization: The Development of Crystalline Order in Thermoplastic Polymers*. Oxford: Oxford University Press, 2001. 140-145.
- [20] Reiter JM, Strobl GR. (eds.) En: *Progress in Understanding of Polymers Crystallization. Series: Lectures Notes in Physics*. Vol. 714, Berlín: Springer, 2007. 481-501.
- [21] Strobl G. A Multiphase Model Describing Polymer Crystallization and Melting. En: *Progress in Understanding of Polymers Crystallization. Series: Lectures Notes in Physics*. Reiter JM, Strobl GR. (eds.). Vol. 714, Berlín: Springer, 2007. 481-503.
- [22] Strobl G. *Eur. Phys. J. E: Soft Matter* 2000; **3** (2): 165-183.
- [23] Muthukumar M, Welch P. *Polymer* 2000; **41** (25), 8333-8337.
- [24] Muthukumar M. *Eur. Phys. J. E: Soft Matter* 2000; **3** (2): 199-202.
- [25] Cheng SZD, Lotz B. *Polymer* 2005; **46** (20): 8662.
- [26] Lorenzo AT, Arnal ML, Müller AJ, Boschetti-de-Fierro A, Abetz V. *Macromolecules* 2007; **40** (14): 5023-5037.
- [27] Lorenzo AT, Müller AJ. *J. Polym. Sci., Polym. Phys.* 2008; **46** (14): 1478-1487.
- [28] Chen HL, Li LJ, Lin TL. *Macromolecules* 1998; **31** (7): 2255-2264.
- [29] Defieuw G, Groeninckx G, Reynaers H. *Polym. Commun.* 1989; **30** (9): 267-270.

- [30] Defieuw G, Groeninckx G, Reinares H. *Polymer* 1989; **30** (12): 2158-2163.
- [31] Hoffman JD. *Polymer* 1983; **24** (1): 3-26.
- [32] Fox TG. *Bull. Am. Phys. Soc.* 1956; **1**: 123.
- [33] Phillips PJ, Rensch GJ, Taylor KD. *J. Polym. Sci. Polym. Phys.* 1987; **25** (8): 1725-1740.
- [34] Phillips PJ, Rensch GJ. *J. Polym. Sci. Polym. Phys.* 1989; **27** (1): 155-173.
- [35] Goulet L, Prud'homme RE. *J. Polym. Sci. Poly. Phys.* 1990; **28** (12): 2329-2352.
- [36] Hoffman JD, Davis GT, Lauritzen JI. En: *Treatise on Solid State Chemistry*, Vol. 3, New York (USA): Plenum, 1976. 497-615
- [37] Cimmino S, Martuscelli E, Silvestre C, Canetti M, De Lalla C, Seves A. *J. Polym. Sci. Polym. Phys. Ed.* 1989; **27** (9): 1781-1794.
- [38] Zhang LL, Goh SH, Lee SY, Hee GR. *Polymer* 2000; **41** (4): 1429-1439.
- [39] Di Lorenzo ML. *Prog. Polym. Sci.* 2003; **28** (4): 663-689.
- [40] Lodge TP, McLeisch TCB. *Macromolecules* 2000; **33** (14): 5278-5284.
- [41] Huang J, Marand H. *Macromolecules* 1997, **30** (4): 1069-1073.
- [42] Alfonso GG, Russell TP. *Macromolecules* 1986; **19** (4): 1143.
- [43] Martuscelli E. *Polym. Eng. Sci.* 1984; **24** (8): 563.
- [44] Shangguan Y, Song Y, Zheng Q. *Polymer* 2007; **48** (15): 4567-4577.