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Tayloring PS/PCL blends: characteristics of processing and properties

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Abstract

Blends of Polystyrene (PS) and Poly(ε-caprolactone) (PCL) were twin screw extruded, two PSs, with low and high melt flow rate (MFR) were used and their feasibility within PCL investigated by means of torque rheometry, mechanical tests, heat deflection temperature (HDT) and scanning electron microscopy (SEM); predictive models were utilized to evaluate interfacial adhesion in PS/PCL blends. Results show that no decreasing was verified in torque rheometry plots suggesting thermally stable blends; elastic modulus decreased and elongation at break increased in PS/PCL blends compared to neat PS. PS/PCL blends with low MFR PS and higher PCL amount are more thermodynamically stable. Higher HDT was verified in PS/PCL blends. The trends observed applying predictive models are indicative of poor adhesion between PCL and PS, agreeing with coalescence and phase segregation as verified in SEM images. PS/PCL systems with higher MFR PS presented the best results.

Keywords: : PS/PCL blends, processing, mechanical properties, predictive models.

1. Introduction

Our society has realized that using persistent polymers for short term applications, which are one kind of main environmental pollution sources, is a misfortune for our planet earth. Nevertheless, not being biodegradable, polystyrene (PS) is currently used in many applications, thereby contributing for the environmental damages (Tokiwa *et al*., 2009; Masek and Zaborski, 2014).

PS is a synthetic polymer made from the monomer styrene. As a thermoplastic polymer, it has a solid (glassy) state at room temperature but flows if heated above about 100°C, its glass transition temperature. It becomes rigid again when cooled. This temperature behavior is exploited for extrusion and also for molding and vacuum forming, since it can be cast into molds with fine detail. PS is an inexpensive resin per unit weight, being one of the most widely used plastics; the scale of its production is several billion kilograms per year. Its uses include protective packaging (such as packing peanuts and CD and DVD cases), containers (such as "clamshells"), lids, bottles, trays, tumblers, and disposable cutlery. As it is non-biodegradable and takes years to degrade, it has contributed to the increase in environmental damages; therefore it is a focus of controversy among environmentalists (Paul and Newman, 1978; Di Lorenzo, 2003; Baltá-Calleja *et al*., 2004; Romeo *et al*., 2009; Shabbir *et al*., 2013).

Polymer blending is a versatile and rather inexpensive method for creating new materials; the desirable properties of the constituent components may be combined without the need to synthesize new macromolecules. Blending cannot only improve properties and processability of existing polymers, but can also reduce the final cost and raise the performance/price balance. The inherent properties of the individual polymer components, the mode of dispersion, shape, size, and orientation of the phases, as well as their interaction, are important factors of the blend's behavior (Paul and Newman, 1978; Uemura and Takayanagi, 1966; Imre *et al*., 2014). Blends with poly(ε -caprolactone) (PCL) appears to be a promising option to modify the PS properties.

PCL is synthetic, biodegradable and biocompatible, it is a widely used commercial biodegradable polymer. Market demand for biodegradable and biocompatible polymers has been rapidly increasing, especially in the packaging and health care sectors, where they are highly encouraged by environmental management policies. However, high cost and low melting temperature (60°C) limit its use for some applications (Broz, *et al*., 2003; Martínez-Abad *et al*., 2013; Lemos and Martins, 2014; Zhou *et al*., 2015; Baker *et al*., 2016), shortcomings that might be fulfilled by blending with PS (Paul and Newman, 1978; Paul, and Barlow,1980; De Kesel *et al*., 1997).

Biresaw *et al*., (2004) observed that PS/PCL systems displayed increased energy absorption and mechanical properties than PS/poly(tetramethylene adipate-co-terephthalate) (PTAT) blends which was attributed to the enhanced compatibility of the PS/PCL blends. Mohamed *et al*., (2007) analysed PS/PCL blends by FTIR, Modulated Differential Scanning Calorimetry (MDSC) and TG. In the FTIR, analyses of chemical interactions indicated that there was a possibility of partial miscibility. Melting and crystallization enthalpies decreased as PS content increased.

Encouraged by the promising properties of PS/PCL systems our research group has been developing these blends (Souza, 2016; França *et al*., 2016; Bezerra *et al*., 2017). Blending PS with PCL can improve some undesirable properties and produce a certain synergistic effect as well. For instance, blending PCL with PS leads to increased Young modulus and allows the use temperature of PCL to be increased; also products made with PS/PCL should be cheaper than those of neat PCL. As PCL is very soft, PS/PCL blends show higher elongation than neat PS.

In the present study, PS/PCL blends were produced by melt mixing; two PSs with different molecular weight (as measured by their melt flow rates - MFR) were used and their properties investigated. The main objective was to manufacture PS/PCL blends with synergic properties to obtain applications that are more widespread. Therefore, PSs with low (4.5 g/10min) and high (17 g/10min) MFR were used and their properties in PS/PCL blends analysed by means of torque rheometry, mechanical properties, heat deflection temperature (HDT), scanning electron microscopy (SEM) and predictive models were also applied to evaluate the interfacial adhesion into PS/PCL blends.

2. Material and method

Crystal Polystyrenes: PS 145D, MFR = 17 g/10 min (200°C/5 kg), density = 1.04 g/cm^3 and PS 158K Q611, MFR = 4.5 g/10 min (200°C/5 kg), density =1.04 g/cm^3, were purchased from Unigel SA. These polystyrenes were coded as PS 145D and PS 158K, respectively. Poly(ε-caprolactone): PCL CAPA 6500, MFR = 28 g/10 min (190°C/2.16 kg), was purchased from Perstorp Winning Formulas.

Blends Preparation

Neat polymers and blends were processed in a twin screw extruder Coperion-Werner & Pfleiderer ZSK 18. Prior to extrusion, the resins were manually cold mixed to promote greater homogeneity. The temperature inside the extruder was kept at 180°C - 200°C and the screw speed was 250 rpm. After extrusion, the material was granulated and oven dried for 24 hours at 40°C. Injected specimens for mechanical, impact and HDT experiments were produced in a FLUIDMEC H 30/40 at 160°C, according to ASTM D638, D256 and D648 standards, respectively. Table 1 presents the compositions investigated in this work.

Compositions	PS (%wt)	PCL (%wt)
PS/PCL (100/0)	100	0
PS/PCL (75/25)	75	25
PS/PCL (50/50)	50	50
PS/PCL (25/75)	25	75
PS/PCL (0/100)	0	100

Table 1
Compositions of the compounds with two PSs with different molar mass studied.

Characterizations techniques

Torque rheometry

Neat polymers PCL, PS 145D and PS 158K and blends PS/PCL were processed in a Haake Rheomix 600 laboratory internal mixer at 50 rpm for 10 minutes, with the chamber wall kept at 200°C. Torque and temperature as function of time were plotted for PCL, PS and PS/PCL blends. Neat polymers PCL, PS 145D and PS 158K and blends PS/PCL were processed in a Haake Rheomix 600 laboratory internal mixer at 50 rpm for 10 minutes, with the chamber wall kept at 200°C. Torque and temperature as function of time were plotted for PCL, PS and PS/PCL blends.

Mechanical properties

Mechanical properties in tension were measured according to ASTM D638; tests were conducted in an EMIC DL 2000 testing machine operating at 5mm/min for PS and its blends; for neat PCL, an elongation rate of 50 mm/min and 200 Kgf load were applied. Impact tests were carried out in a CEAST Resil-5.5 impact machine operating with a 2.75 J pendulum on notched specimens in Izod configuration, according to ASTM D256. Presented results are an average of seven experiments.

Flexion tests at three points for PS/PCL blends and neat polymers, were performed in a Shimadzu Autograph AG-X 50kN operating at a displacement rate of 1.6 mm/min with a distance between grips of 50 mm. Presented results are an average of four experiments.

Predictive modeling

Predictive models were used to evaluate the theoretical elastic modulus of binary blends, it was done in order to access the interfacial linkages between the components of PS/PCL blend (models with perfect adhesion as well as models where adhesion is absent), and then to compare with those results experimentally obtained. In the subsequent paragraphs, the models used in this study are briefly described.

Rule of the mixture: considers perfect adhesion between matrix and dispersed phase and perfect dispersion of spherical inclusions into the matrix, its parameters can be determined according to Equation 1 (Cohen and Ishai, 1967; Tomar and Maiti, 2007):

$$E_b = \left[\left(\frac{E_d}{E_m} - 1\right) \times \emptyset_d + 1\right] \times E_m \quad (1)$$

Where: E_b is the blend elastic modulus, E_d is the dispersed phase elastic modulus, Em is the matrix elastic modulus and $\emptyset_d$ is the free volume fraction of the dispersed phase.

The volumetric fraction of the dispersed phase was calculated according to Equation 2, following approaches (Nielsen, 1970; Romeo *et al.*, 2009):

$$\emptyset_d = \frac{c\rho_m}{\rho_d + c\,(\rho_m + \rho_d)} \quad (2)$$

Cohen and Ishai Model: the dispersed phase is regarded as a phase that does not interact, being equivalent to a pore or hollow (Romeo *et al.*, 2009):

$$E_b = (1 - \emptyset_d^{2/3}) \times E_m \quad (3)$$

The above described variables have the same definition in all models used in this work.

Kerner-Uemura-Takayanagi (KUT) Model: considers the dispersed phase as spherical inclusions with E_d into a continuous matrix with E_m, and Poisson's ratio of the matrix (νm) is assumed as 0.5. This model has two branches (Kerner, 1956; Broz *et al.*, 2003; Zhou *et al.*, 2015):

1) Perfect adhesion at blend interface (KUT1), Equation 4:

$$E_b = E_m \left[\frac{(7\text{-}5\nu_m) \times E_m + (8\text{-}10\nu_m) \times E_d - (7\text{-}5\nu_m)\,(E_d\text{-}E_m) \times \emptyset_d}{(7\text{-}5\nu_m) \times E_m + (8\text{-}10\nu_m) \times E_d + (8\text{-}10\nu_m)\,(E_d\text{-}E_m) \times \emptyset_d}\right] \quad (4)$$

2) Absent interaction at blend interface (KUT2), Equation 5:

$$E_b = E_m \left[\frac{(7-5\nu_m) \times E_m - (7-5\nu_m) \times E_m \emptyset_d}{(7-5\nu_m) \times E_m + (8-10\nu_m) \times E_m \emptyset_d} \right] \quad (5)$$

Heat deflection temperature (HDT)

Heat deflection temperature tests carried out in a HDT 6 VICAT P/N 6921.000 instrument according to ASTM D648. Experiments were conducted at load 1820 KPa for PS and its blends and for neat PCL at load 455 kPa, the heating rate was 120 °C/h, specimens were immersed into silicone bath oil. HDT was determined at 0.25 mm of specimen deflection. Presented results are an average of three tests.

Scanning electron microscopy (SEM) images

SEM images were obtained in a SSX 550 Superscan - Shimadzu equipment operating at 10 kV, under high vacuum. Fractured impact sample tests were used, their surfaces were gold coated using a Shimadzu sputter IC 50, operating with a 4 mA current for a period of 2 minutes, which was done in order to avoid negative charge accumulation.

3. Results and discussion

Torque rheometry plots

Figure 1 shows torque versus time plots of neat PS 145D, PS 158K, PCL and blends. As can be seen in Figure 1 (c) PS 158K showed a higher torque, which is most likely due to the higher viscosity (MFR = 4.5g/10min) when compared to PS 145D (MFR = 17g/10min) and PCL (MFR = 28 g/10 min). Figure 1 (b, d) presents a zoom between 9 – 10 min. For the terminal processing stage, a stabilization of the torque is visible, suggesting absence of resin degradation during processing. Consequently, the morphological characteristics are associated to the chemical interaction, phase coalescence, and miscibility mechanisms between PCL and PS, as further presented by mechanical properties (see Figure 4 and Tables 2) and SEM images (see Figures 2 and 3).

Increasing the PCL content of the blends promotes a decrease in the torque and consequently in the blend viscosity. Possibly, this reduction is due to the lower viscosity of PCL in this temperature range, which contributes to a decrease in the viscosity of PS/PCL system as a whole. An even more pronounced decrease was observed for PS 145D, which can be linked to the higher PS 145D MFR compared with that for PS 158K.

Upon decrease of the viscosity with temperature, in every system some phenomena emerge, among them, an increase of free volume between molecules, increasing molecular vibration, and decreasing intermolecular contacts between polymer chains (Bretas and D'avila, 2000).

In the present situation, the torque initially diminished during the feeding stage, and then a constant plateau is defined until the end of processing. Blends with higher PCL content presented lower torque values possibly due to their higher MFR (28 g/10 min). After the feeding stage, no decreasing was observed in torque plots for the neat resins and blends making sure that degradation reactions did not take place during processing (Utracki, 2002; Agrawal *et al.*, 2008).

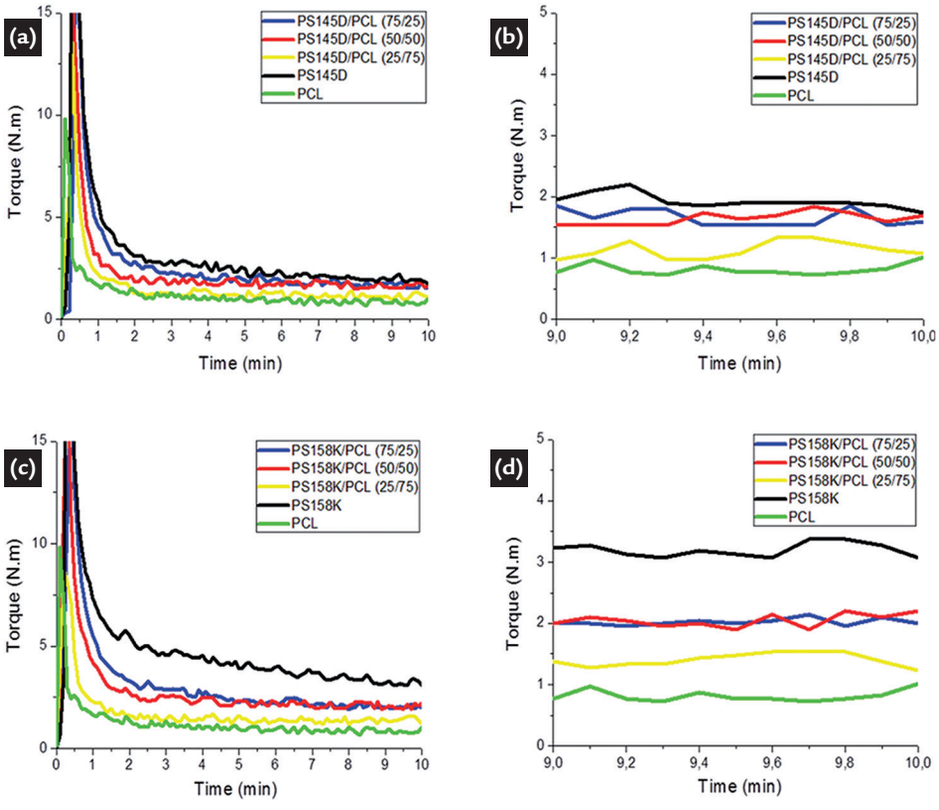

Figure 1
Torque versus time plots for PS, PCL and PS/PCL blends, (a) PS 145D and (b) on the right side is a zoom of torque plotted between 9 and 10 minutes of processing of PS 145D, (c) PS 158K and (d) on the right side is a zoom of torque plotted between 9 and 10 minutes of processing of PS 158K.

Scanning Electron Microscopy (SEM) Images

In Figures 2 and 3 are SEM images of the impact fractured surface of PS/PCL blends. In all blends, one may observe the presence of heterogeneous phases, in which PCL is the dispersed phase visualized as spherical particles and PS is the continuous phase. It is observed that the blends with 25% PCL present smaller particles (see Figures 2a and 3a) when compared to the blends with 50% of PCL content; larger PCL particles in 50/50 blends suggest that coalescence and segregation mechanisms took place. In these SEM images, PCL particles were plucked from PS matrix after which PS presented smooth surfaces, also indicating poor interfacial adhesion between PCL and PS. (Paul and Barlow, 1980; Baker *et al.*, 2016). Regarding the PSs used, PS 158K presented bigger particles as presented in Figure 3. This is a consequence of phase coalescence due to lower chemical interactions (Olabisi *et al.*, 1979; Utracki, 2002).

Upon increasing PCL content, the dispersed phase remained as PCL, and PS was the continuous phase. There is still a great heterogeneity regarding the size of these domains, with particles ranging from 10 to 2 µm (indicated by red arrows in the Figures). This heterogeneity was more evident for the PS158K matrix, possibly due to the higher difference between the melt flow rates (PCL is 28g/10 min, PS 145D is 17g/10 min and PS 158K is 4.5g/10min). Particles with large sizes, in the micron order are indicatives of polymeric systems with low miscibility, leading to weaker mechanical properties. Considering the influence of viscosity, PS145D/PCL blends with higher MFRs and the spherical particles have smaller sizes (indicated by arrows) and superior mechanical properties; these are evidences of polymeric systems with improved compatibility.

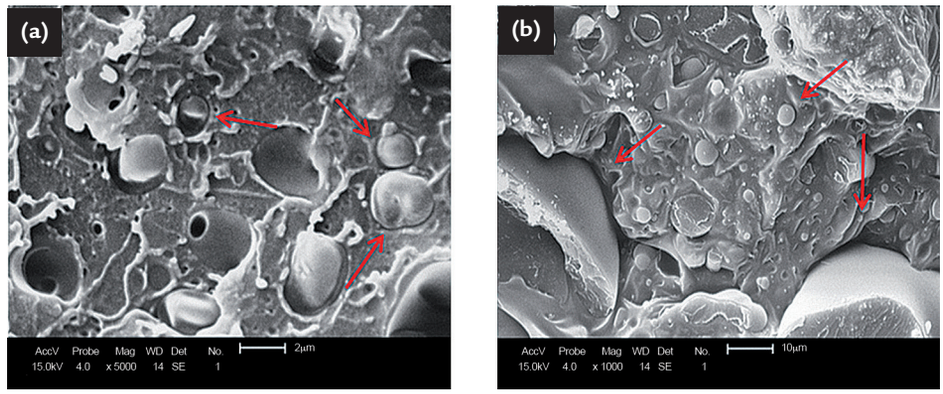

Figure 2
SEM images of fractured surface. (a) PS 145D/PCL (75/25), (b) PS 145D/PCL (50/50).

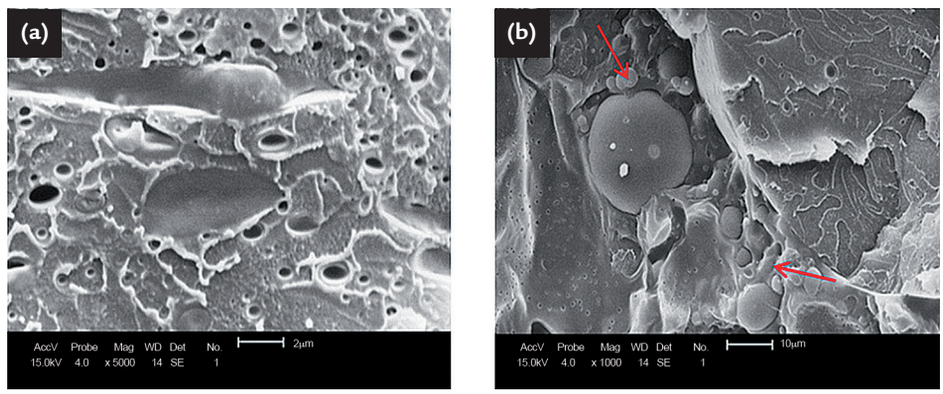

Figure 3
SEM images of fractured surface: (a) PS 158K/PCL (75/25), (b) PS 158K/PCL (50/50).

Mechanical Properties

Mechanical properties in tension for PS 145D, PS 158K, PCL and PS/PCL blends are presented in Table 2. It's observed that both polystyrenes exhibited elastic modulus and elongation at breakage, characteristic of fragile polymers; meaning low deformation before fracturing. The results reported in herein are higher than those provided by the manufacturer (Elastic Modulus, 50 and 40 MPa, for PS 158K and PS 145D respectively and Elongation at breakage, 2.5 and 1.5 %, for PS 158K and PS 145D, respectively). This is most likely due to the proper processing parameters used in this study.

Neat PCL showed lower elastic modulus and higher elongation, characteristic behavior of ductile material, such as PCL at room temperature (~23°C). Computed results for neat PCL agree with those reported in literature (Simões *et al.*, 2009). Upon addition of PCL to the PS matrix, a considerable decrease in the elastic modulus and in the tensile strength was found. For PS 145D/PCL (75/25) blends, it diminished by 47.4% and 47.2 %; for PS 145D/PCL (50/50), it diminished by 63.2% and 63%; for PS 158K/PCL (75/25), it diminished by 67.9% and 65.1% and for PS 158K/PCL (50/50), 72.5% and 70.1% respectively; the values getting closer to those of neat PCL. This result might be associated to the low adhesion between the PS and PCL phase, avoiding proper charge transference in the blends.

Regarding the results for elongation at breakage, no significant differences were observed for PS/PCL blends compared with those obtained for neat PS. It may be assumed that this result is with low adhesion as well as with high interfacial tension between PS and PCL phases, and it agrees with the SEM images (Figures 2 and 3).

PS and PCL do not exhibit similar functional groups. Besides, PCL contain carbonyl groups, which are quite polar; only secondary chemical interactions are expected for these blends, resulting in weak

interfacial adhesion, which may lead to low mechanical properties. Coalescence and phase segregation phenomena are expected to happen. SEM images showed (Figures 2 and 3) PCL have larger spherical particles in PS/PCL 50/50 blend. Possibly, due to phase coalescence; this behavior may explain the mechanical properties obtained in this study (Olabisi *et al.*, 1979; Souza, 2016).

Table 2
Mechanical properties for PS 145D, PS 158K, PCL and PS/PCL blends.

Compositions*	Elastic Modulus (GPa)	Tensile Strength (MPa)	Elongacion at Break (%)	Impact strength (J/m)	Elastic Modulus under Flexion (GPa)	Tensile strength under flexion (MPa)
PS 145D	0.95 ± 0.05	34.7 ± 1.1	5.1 ± 0.4	18.03 ± 0.82	1.06 ± 0.07	41.02 ± 2.68
PS 145D/PCL (75/25)	0.50 ± 0.05	18.3 ± 1.1	4.7 ± 0.3	18.92 ± 0.75	0.90 ± 0.07	23.90 ± 1.34
PS 145D/PCL (50/50)	0.35 ± 0.04	12.8 ± 0.7	6.1 ± 0.5	18.71 ± 1.09	0.45 ± 0.03	15.41 ± 0.35
PS 158K	1.09 ± 0.08	40.5 ± 2.4	6.0 ± 0.7	27.31± 0.77	2.69 ± 0.12	79.15 ± 2.64
PS 158K/PCL (75/25)	0.35 ± 0.03	14.1 ± 2.1	6.2 ± 0.1	16.25 ± 0.43	0.75 ± 0.01	18.16 ± 1.35
PS 158K/PCL (50/50)	0.30 ± 0.02	12.0 ± 0.5	6.5 ± 0.6	16.46 ± 0.71	0.53 ± 0.02	12.94 ± 0.39
PCL	0.23 ± 0.02	18.8 ± 1.7	> 418.0**	239.0 ± 9.9	0.39 ± 0.01	28.18 ± 0.28

*PS 145D/PCL (25/75) and PS 158K/PCL (25/75) specimens were not successfully injected, possibly due to MFR difference.

** Specimens did not break during the experiment.

For the results for the impact strength of PS 145D, PS 158K, PCL and PS/PCL blends in Table 2, one can verify excellent impact strength for neat PCL, which is due to its ductile behavior. It is also observed that addition of PCL into the PS 145D matrix did not promote a significant increase in PS impact strength. For the blends with PS 158K, a decrease around 40% was observed when compared with neat PS 158K. In general, the results did not follow a linear increasing trend upon PCL addition to PSs. These lower impact strength results are possibly linked to a poor PS/PCL interphase, which means PS and PCL have few molecular interactions and high interfacial tension, acting as a barrier to the tension transfer between PS and PCL phases. Perhaps addition of a compatibilizer with reactive groups between PCL and PS maybe contribute to a decrease of tensions, strengthening the interfacial region and increasing energy absorption mechanisms; thus promoting the miscibility and compatibility of PS/PCL blends. Results verified for impact strength are consistent with those presented in Figure 4, where according to predictive models PS/PCL blends have low adhesion at interphase, as well as with SEM images presented in Figures 2 and 3.

Table 2 shows the results for elastic modulus and tensile strength under flexion experiments for PS 145D, PS 158K, PCL and PS/PCL blends. It is observed that there is a decrease in the elastic modulus of PSs upon addition of PCL, with the values ranging from 15% to 57% for PS 145D/PCL (75/25) and (50/50), respectively, and from 72% to 80% for PS 158K/PCL (75/25) and (50/50), respectively. Regarding the results for tensile strength, they are between 40-80% lower for the blends compared with those for the neat PSs. On the other hand, looking at neat PCL, elastic modulus increased upon addition of PS. Nevertheless, like the tensile strength test, the results for the flexion strength test are more sensitive to interfacial adhesion in the blend. Consequently, the results presented suggest a poor adhesion between the polymers, reinforcing the results obtained with the predictive models as seen in Figure 4. According to Paul *et al.* (1978), polymeric chains with lower molecular weight polymer chains are more likely to produce miscible systems than molecular weight because of the greater ease of diffusion. This argument agrees with the present situation. PS 145D with higher MFR and lower viscosity presented the best results, possibly due to the higher interaction amount present in PS 145D/PCL blends.

To analyze the compatibility of PS/PCL blends, several predictive models were used. The results are in the following section.

Predictive modeling

Figure 4 shows the experimental and theoretical results measured using the predictive models for PS 145D/PCL and PS 158K/PCL blends, respectively. It is worth mentioning that during theoretical calculations for PS/PCL blends with PCL content equal or lower than 50 wt%, the PS was assumed as being the continuous phase, i.e. the matrix; this consideration is in agreement with the morphology observed by SEM images (Figures 2b and 3b).

According to results presented, it is observed that the Elastic Modulus for PS/PCL blends as well as for PS 145D and PS 158K matrixes is closer to the Cohen and Ishai (1967) and KUT2 (Kerner, 1956; Uemura and Takayanagi, 1966) models. The trends observed applying these models are indicative of poor adhesion between the PCL and PS phases, since they consider zero adhesion between the phases.

The results shown in Figure 4 agree with the predictions of low chemical interactions between PS and PCL, with phase coalescence as shown in SEM images. Among obtained results, PS 145D showed a better fit with Cohen and Ishai and KUT2 models than PS 158K. It is speculated that the low viscosity of PS 145D (high MFR) is associated with better wettability of PCL chains, and lower degree of coalescence and separation of phases, which would provide a better match with the Cohen and Ishai and KUT2 models.

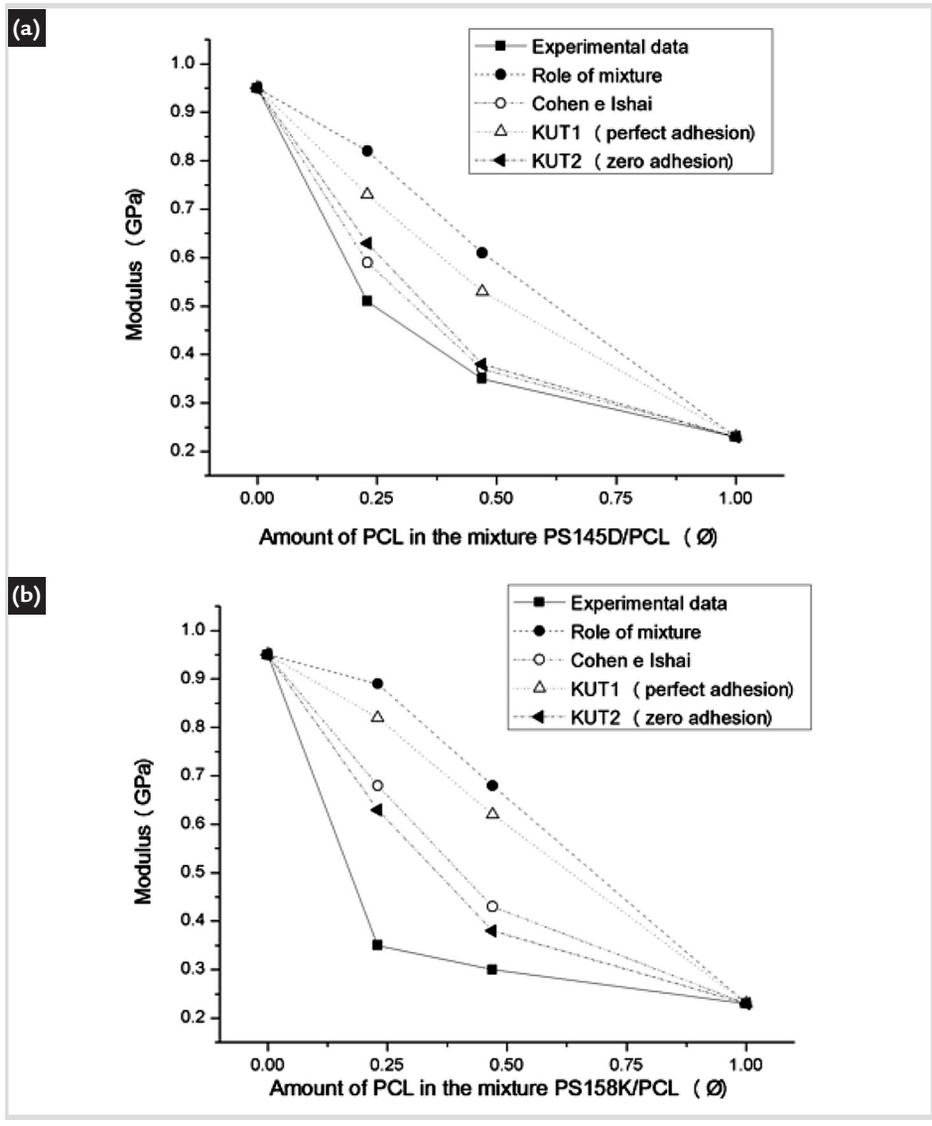

Figure 4
Plots of experimental and theoretical elastic modulus: (a) PS 145D and PS 145D/PCL blends; (b) PS 158K and 158K /PCL blends. (Theoretical models are indicated).

Heat deflection temperature (HDT) measurements

Table 3 shows heat deflection temperature results for the polystyrenes and their blends with PCL. There is observed a decrease in the HDT values for PS/PCL blends of 11.5% and 28.1% for PS 145D/PCL, 75/25 and 50/50 respectively, and of 15.0% and 30.9% for PS 158K/PCL, 75/25 and 50/50, respectively, when compared with values of neat PSs. On the other hand, there was verified an increase on the HDT values of PCL upon addition of PS, increases of 58.1% and 28.4% were observed for the compositions with PS 145D/PCL with 75/25 and 50/50, respectively, and for PS 158K/PCL increases of 56 % and 27,9% for 75/25 and 50/50, respectively. Once more, decrease in mechanical properties was higher for the blends with PS 158K; it seems that PS 145D, with lower viscosity, has a better grip with PCL. It is also possible that the smaller polymeric chains of PS 145D present greater miscibility with PCL (Olabisi *et al.*, 1979). Summing up, these results suggest that products made with PS/PCL blends can be used at higher temperatures than those made with neat PCL.

Table 3
Heat deflection temperature (HDT) measurements for PS 145D, PS 158K, PCL and PS/PCL blends.

Compositions	HDT (°C)
PS145D	74.1±0.9
PS 145D/PCL (75/25)	65.6 ±1.8
PS 145D/PCL (50/50)	53.3 ±0.06
PS 158K	76.9 ± 0.5
PS 158K/PCL (75/25)	64.8 ± 0.8
PS 158K/PCL (50/50)	53.1 ± 1.1
PCL	41.5 ± 1.9

4. Conclusions

Blends of PS/PCL were successfully prepared in this study; the processing parameters tested are appropriate for

producing thermally stable blends without any degradation reaction taking place. PS with higher MFR provides blends with specific properties, such as mechanical properties involving: modulus, impact strength, tensile strength under flexion. Between the predictive models applied, Cohen and Ishai; and KUT2 models presented the best fits; they assume poor adhesion between the PCL and PS phases, agreeing with coalescence and phase segregation as verified in SEM images and low mechanical properties of these systems. The addition of a compatibilizer with reactive groups between PCL and PS maybe contribute to an increase the miscibility and compatibility of PS/PCL blends.

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