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Polymer 42 (2001) 8415–8424

polymer

www.elsevier.nl/locate/polymer

Orientation of uniaxially stretched poly(vinyl phenol)/ poly(vinyl methyl ether) blends

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Received 2 March 2001; received in revised form 4 May 2001; accepted 7 May 2001

Abstract

Orientation of poly(vinyl phenol) (PVPh)–poly(vinyl methyl ether) (PVME) amorphous miscible blends has been studied using FTIR spectroscopy. Blends of 33, 42, 53 and 66% (mol/mol) in PVPh were uniaxially stretched at 0.1 s^{-1} and $T_g + 15$. Both polymers showed similar orientation values in the blend. Whereas, at high PVPh concentration, the orientation function $\langle P_2 \rangle$ is linear with deformation, at intermediate compositions a non-linear relationship was observed, attributed to a fast relaxation. Orientation of both polymers increases with PVME concentration up to 48 mol% (40 wt%) composition. For blends richer in PVME, orientation decreases. It is proposed that the maximum in orientation is related to the presence of strong intermolecular PVPh–PVME hydrogen bonds, which hinder relaxation and increase the friction coefficient. Comparison with PVPh–poly(methyl methacrylate) and PVPh–poly(ethylene oxide) blends, which are both hydrogen bond containing systems, suggest that hydrogen bonds hinder relaxation and could favor cooperativity. Moreover, comparison to poly(styrene)–poly(vinyl methyl ether) blends, a similar system that does not present hydrogen bonds and that was studied by various groups previously, shows that the maximum in orientation is related to interaction fluctuations. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl phenol); Poly(vinyl methyl) ether; Hydrogen bonding

1. Introduction

Polymer blending is one of the routes used to create made-to-measure materials. In all but a few rare instances, miscibility is observed only when there is significant interaction between constituent polymers. Interactions can be of different type and strength, e.g. van der Waals attractions (weak, of the order of 0.2 kcal mol^{-1}), hydrogen bonds (medium, typically in the 1–10 kcal mol^{-1} range) or ionic interactions (strong, of the order of 50 kcal mol^{-1}).

Unfortunately, polymer blend properties seldom follow simple additive laws. In particular, orientation, which controls to a large extend the ultimate properties of the material, often eludes prediction. Many factors can be invoked to explain this fact.

Firstly, the orientation process itself cannot be isolated. Chain orientation is always followed by relaxation phenomenon that can be reduced to a certain extend (e.g. quenching), but that cannot be completely suppressed. Therefore, analysis of orientation results is strongly dependent on the study of the effect of relaxation on the final measurements.

Secondly, the role that interactions play in orientation and relaxation processes has not been completely elucidated. Attempts to rationalize the orientation behavior do not apply to all polymer systems. For example, Jasse et al. [1] proposed that strongly interacting blends (with negative interaction parameter χ) correspond to cases where orientation varies linearly with composition for polymers forming the major component of the blend, although the trend is not applicable to the middle composition range. This feature was found true for poly(styrene)–poly(2,6-dimethyl-1,4-phenylene oxide) (PS/PPO) and poly(styrene)–poly(methyl methacrylatate) (PS/PVME) blends for PS [1], and for poly(methyl methacrylate)–poly(ethylene oxide) (PMMA/PEO) blends for PMMA [2]. However, for poly(vinyl chloride)/poly(α-methyl-α-*n*-propyl-β-propilactone) (PVC/PMPPL) [3], which forms hydrogen bonds, a nonlinear behavior is reported. Moreover, Jasse et al. [1] suggested that interactions hinder relaxation, leading to an increase in orientation. The slowing down of relaxation has been related to an increase in the friction coefficient ξ, due to a decrease in chain mobility. In addition, it has been pointed out that strong interactions may play the role of effective cross-links, modifying the density of chain entanglements [4]. In this context, Bazuin et al. [5] reported that hydrogen bonds involving carboxylic groups did not influence orientation of blends

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PII: S0032-3861(01)00355-X

of poly(styrene-*co*-4vinyl pyridine) (PS-VP) with poly(styrene-*co*-methacrylic acid) (PS-MAA) copolymers for up to 12%. Nevertheless, in the same work it is concluded that the sulfonic groups of poly(styrene-*co*-styrene sulfonic acid) (PS-SSA), forming stronger hydrogen bonds, would be responsible for a substantial orientation increase as compared to poly(styrene). Furthermore, in the case of PS-SSA with PS-VP blends, hydrogen-bonded ion–ion interactions would be responsible for an increase in orientation, acting as effective cross-links in the time scale of the experiments.

In order to gain insight about the role of interactions in orientation, our research group has focused on the effect of hydrogen bond interactions on orientation. We have chosen to work with poly(vinyl phenol) (PVPh), whose repeat unit is very close to that of poly(styrene), but which bears a hydroxyl group in the *para* position of the aromatic group. This hydroxyl function imparts to PVPh the ability to form hydrogen bonds with itself (which will be called intramolecular bonds) and with other polymers (referred to as intermolecular bonds). Li and Brisson have studied the orientation of pure PVPh [6] and also of the poly(vinyl phenol)–poly(methyl methacrylate) (PVPh/PMMA) system [7]. It was found that PMMA orientation decreased with addition of PVPh, whereas PVPh orientation increased, pure PMMA orientation being superior to that of PVPh.

Rinderknecht and Brisson [8] have studied the orientation in the poly(vinyl phenol)–poly(ethylene oxide) (PVPh/PEO) blends. Contrarily to PVPh/PMMA, in this system intermolecular hydrogen bonds (PVPh–PEO) are stronger than intramolecular (PVPh–PVPh) hydrogen bonds [9,10]. Whereas almost no orientation was reported for PVPh, PEO showed a maximum in orientation at a composition close to a 1:1 mole ratio of interacting units, which was attributed to the formation of strong hydrogen bonds.

In this work, we present the orientation of poly(vinyl phenol)–poly(vinyl methyl ether) (PVPh/PVME) blends. This system has been chosen because it presents strong intermolecular hydrogen bonds but of lesser strength that those in PVPh/PEO blends [9,11]. Therefore, the comparison with previously studied systems will allow to explore the relationship the between the strength of hydrogen bonds and orientation. Furthermore, orientation of PS/PVME, a structurally similar system that does not contain hydrogen bonds, has been extensively reported in the literature [12–16], therefore the comparison with PVPh/PVME blends is proposed to gain insight about the role of interactions on orientation.

2. Experimental

The materials used in this study were poly(vinyl phenol) (PVPh) from TriQuest and poly(vinyl methyl ether) (PVME) from Aldrich. PVPh had a M_w of 29,300 g mol^{-1} and polydispersity index of 2.9, as determined by size exclusion chromatography (SEC) curves provided by the supplier. PVME had a M_w of 111,000 g mol^{-1} and a polydispersity of 2.4, determined by SEC using an apparatus equipped with a refractive index detector Optilab 903 from Wyatt and a Shodex and a PLgel columns. The measurements were done using tetrahydrofuran as a solvent and PS standards, at 25°C.

PVPh/PVME blends were prepared by dissolving both polymers into acetone in a 2–8% (w/v) concentration. Partial solvent evaporation was performed using a rotary evaporator to increase the concentration to higher values for film casting. Molar and weight percentages of PVPh and PVME for the different blends prepared are shown in Table 1. For brevity purposes, blends will be referred to by their molar percentage in PVPh, unless otherwise stated.

Thin films (~20 μm) were cast onto poly(ethylene) surfaces from PVPh/PVME solutions of concentrations of approximately 70% (w/v). In all cases, film thickness was selected so that the maximum in absorbance of the vibrations under study did not exceed 1.0, in order to remain within the limits of the Beer–Lambert law. The resulting films were cut into strips and two pieces of Pyrotype (Aremco) were attached to the extremities, in order to prevent slippage during stretching. The films were air-dried for 24 h, followed by drying under vacuum at T_g + 12 for 4 days to remove solvent traces and residuals stresses. This drying temperature was selected to minimize thermal degradation. During the drying period, DSC scans were measured every day and care was taken to verify that no changes in T_g were detected and no sign of solvent evaporation were recorded in the first DSC scan at the end of the drying period. Samples were kept under dynamic vacuum in a dessiccator after drying to insure that no moisture absorption occurred. Glass transition temperatures (T_g) of the blends were determined using a Perkin–Elmer DSC-7, calibrated with indium, at a heat rate of 10 K min^{-1}. The T_g values were calculated as the midpoint of the transition in the second recorded scan. Only one T_g was found for each blend and no melting peaks were observed, confirming that the blends were miscible and amorphous, as previously reported in the literature [9,11,17,18]. Glass transition widths were composition independent for the studied blends. This result is in agreement with experimental works reported earlier [11] and with spinodal phase diagram calculations, which predict a single-phase region for this system, implying that it is theoretically miscible throughout

Table 1
PVPh/PVME blends used in this work

Sample	PVPh/PVME (mol%)	PVPh/PVME (wt%)	$T_g \pm 1.5$ (°C)
PVPh66%	66/34	80/20	137
PVPh53%	53/47	70/30	109
PVPh42%	42/58	60/40	81
PVPh33%	33/67	50/50	65

the entire temperature range considered [18]. The glass temperatures for the different PVPh blends are given in Table 1.

Molecular orientation was induced through uniaxial extension at $T_g + 15°C$. Stretching of the films (20 × 10 mm strips) was performed by using an apparatus constructed in our laboratory (described elsewhere [6]), at an exponential rate of 0.1 s^{-1}. Before drawing, the sample was kept at the stretching temperature for a period of 30 min to allow thermal equilibration. After stretching, the sample was quenched to room temperature using an air-fan fed with liquid nitrogen vapors. A maximum of 2–3 s passed between the end of stretching and the freezing-in of orientation at temperatures below the sample T_g.

Deformation of the samples was characterized as the draw ratio, λ, i.e. ratio between final and initial length. The actual draw ratio and the uniformity of stretching were monitored by ink marks drawn along the side of each film before stretching.

Infra-red dichroism measurements (FTIR) were performed using a Nicolet Magna-IR® 560 equipped with a MCT/A detector and a polarizer. For each spectrum, 200 scans were taken at a resolution of 4 cm^{-1}. Oriented films were rotated by 90° to obtain the spectra parallel and perpendicular to the draw direction of the sample. The measured absorbances were used to calculate the dichroic ratio $R = A_{\parallel}/A_{\perp}$.

The orientation was characterized as the second-order moment of the orientation function $\langle P_2(\cos\theta)\rangle$, abbreviated $\langle P_2\rangle$ throughout the text, and it was calculated using the following equation [19],

$$\langle P_2(\cos\theta)\rangle = \frac{(R-1)}{(R+2)}\frac{(R_0+2)}{(R_0-1)} \tag{1}$$

θ being the angle between the chain axis and the stretching direction, and $R_0 = 2\cot^2\alpha$, where α is the angle between the polymer chain axis and the dipole transition moment vector of the vibration considered.

The vibrations chosen for the dichroic analysis are shown in Fig. 1. Analysis of the PVPh orientation in the blend was done using the absorption band located at 3021 cm^{-1}, which is assigned to aromatic CH stretching vibration modes. Rinderknecht and Brisson [8] estimated for this vibration an α angle of 90° for PVPh/PEO blends, using PVPh dichroic measurements reported previously [6]. The dichroic ratio of this vibration was determined using a baseline defined from 3051 to 2996 cm^{-1}. The hydroxyl stretching vibrations, which span from 3353 to 3326 cm^{-1}, were used to investigate orientation of hydrogen bonds.

The vibration at 785 cm^{-1} has been assigned to rocking of the CH_2 group of PVME [20] and was used for orientation determination. Based in geometrical considerations, the α angle was estimated to be 90°.The 785 cm^{-1} vibration is a shoulder of the 830 cm^{-1} band attributed to PVPh in the blends studied. Spectra of the 880–750 cm^{-1} region were analyzed applying a two-points baseline and the curve-fit functions of GRAMS/386 software. Once the baseline was defined, the AutoFind option of the curve-fit function was used to obtain a first guess of the peaks. Three peaks with FWHH (peak full width at half height value) of 6,460 and a gaussian fit were selected, no other peak parameters were fixed. Once the first estimation was obtained, a maximum of 50 iterations was allowed to converge to a minimum solution. Deconvolution of the absorption bands led to three well defined bands situated at 830, 810 and 785 cm^{-1} with an average square regression coefficient of 0.998. A typical example is shown in Fig. 2. Dichroic ratio calculated for the deconvoluted 785 cm^{-1} band using a height ratio were the same than those obtained for the original spectra for the same band when using a baseline defined from 875 to 763 cm^{-1} and a height ratio, obtaining a linear relationship with draw ratio. Therefore, this last methodology was used to calculate PVME orientation in the blends. This procedure was successful for all the blends with the exception of the PVPh66% films, where the low composition in PVME did not allow obtaining a satisfactory fit.

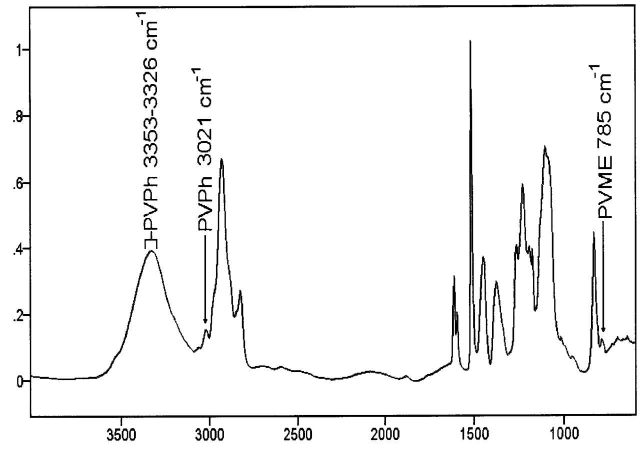

Fig. 1. FTIR spectrum of the PVPh/PVME blend with 33 mol% PVPh composition. Vibrations selected for orientation determination are signaled.

Error associated with the orientation value was calculated as the standard error. For each sample, measurements were

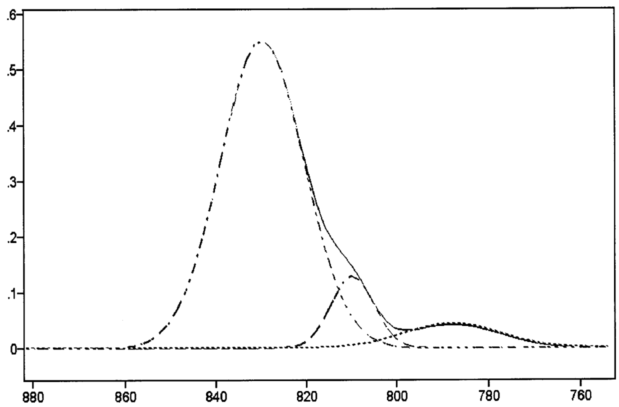

Fig. 2. Example of deconvolution of 830, 810 and 785 cm^{-1} bands for 33 mol% PVPh composition.

performed on three different positions of the sample. Each $\langle P_2 \rangle$ value reported represents the average among 3–6 different samples and 9–18 measurements.

$\Delta P_2/\Delta\lambda$ values, which are the values of the slopes of $\langle P_2 \rangle$ vs. λ plots, were obtained by fitting the experimental curves to linear polynomial (for linear plots) or to two parameter exponential rise (for non-linear plots) equations using SigmaPlot 5.00 and evaluating their analytical derivative at $\lambda = 1.5$ and 3.0.

Error in α angle estimation of the hydrogen bonded vibration of PVPh was determined from statistical treatment of the slope of $\langle P_2 \rangle$ for 3021 cm^{-1} vibration vs. $(R+1)/(R+2)$ of the ν(O–H) bonded hydroxyl vibration for the different blends. For each composition, this statistical treatment consisted in applying the Student's test with a 95% confidence level to the slope value to obtain the two end points for the interval. By applying Eq. (1) to these values, the α angles were calculated. Error was estimated by defining two end point α angles with a 95% confidence level. The half of the difference between both α values was reported as the error.

3. Results and discussion

Elucidation of the orientation behavior of blends is, as will be seen, far from being straightforward. In order to simplify the interpretation, all systems discussed in the present article, unless otherwise stated, refer to compositions where only one phase is present. All blends studied or discussed from the literature were therefore miscible and amorphous to the best of our knowledge.

3.1. Orientation of PVPh/PVME system

Orientation of the PVPh component of PVPh/PVME blends is reported in Fig. 3. As can be seen, orientation increases with draw ratio for all blend compositions, which is the expected behavior for amorphous polymers [1]. For blends rich in PVPh (PVPh66 and PVPh53%), orientation increases linearly with draw ratio. For PVPh42 and PVPh33% blends, there is a non-linear $\langle P_2 \rangle$ vs. λ relationship. This suggests that, as drawing time increases (higher λ), relaxation competes successfully with orientation, reducing the final orientation value observed. Similar non-linear behavior at high deformations has been already reported by Abtal and Prud'homme for PS in amorphous blends with PVME [14] and by Rinderknecht and Brisson PEO in amorphous PVPh/PEO blends [8].

Fig. 4 shows the orientation of the second component of the blends, PVME, as a function of draw ratio for the different blend compositions. As mentioned in Section 2, the only vibration, which allowed measurement of PVME orientation in the blends was partially overlapped with a PVPh vibration, preventing orientation determination for the PVPh66% composition. For all measurable compositions, it can be seen that orientation increases with deformation

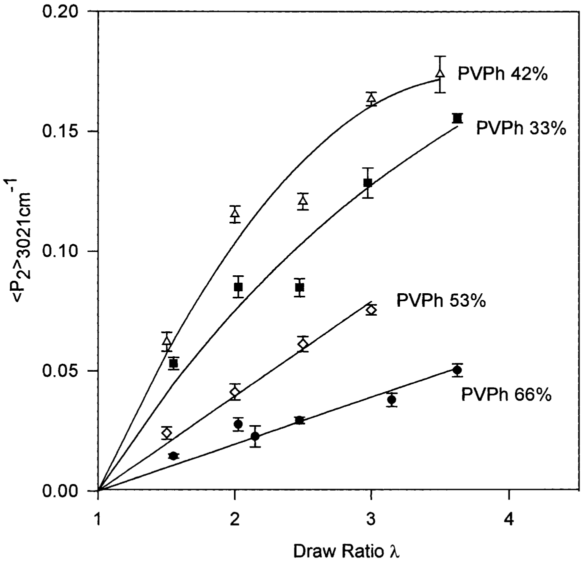

Fig. 3. PVPh orientation of PVPh/PVME blends for different blend composition as a function of draw ratio.

in all cases. Whereas for PVPh53%, a linear trend is observed, in blends richer in PVME, orientation shows a non-linear behavior. This is noteworthy, as in PS/PVME blends, PVME is only very slightly oriented, as verified by the low values of the PVME contribution to the blend total birefringence [14]. This could be due to the higher molecular weight used here as compared to that in the PS/PVME system, which was 44,000 g mol^{-1}. However, the difference between both blends can also be explained qualitatively by the presence of strong hydrogen bonds in PVPh blends. These can hinder relaxation, acting as effective cross-links and increasing the friction coefficient. This behavior is similar to that observed for PEO in PVPh amorphous

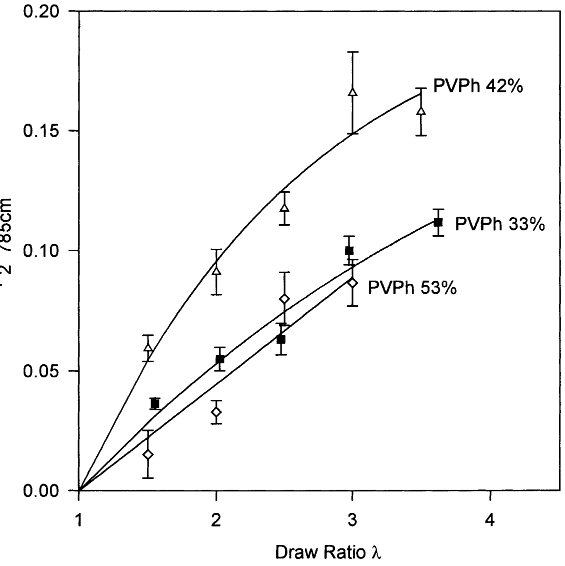

Fig. 4. PVME orientation of PVPh/PVME blends for different blend composition as a function of draw ratio.

blends [8]. PEO attained relatively high orientation values (up to 0.14 for $\langle P_2\rangle$ at $T_g + 10$) when blended with PVPh, contrarily to PEO/PMMA amorphous blends [2], where no orientation was observed for PEO. It was proposed that PEO relaxation was considerably slowed down by hydrogen bonds.

It is useful to characterize orientation using the slope of $\langle P_2\rangle$ curves, $\Delta P_2/\Delta\lambda$, against blend composition [21]. This is often used to compare orientation vs. composition in the blends. Since a high draw ratio corresponds to a longer experimental lapse of time, $\Delta P_2/\Delta\lambda$ is a measure of how easily or how fast polymer chains will orient. As mentioned in Section 1, the final orientation is always the sum of two competing processes: orientation induced by deformation and relaxation that occurs before the stretched sample is quenched. Therefore, a low value of $\Delta P_2/\Delta\lambda$ can be interpreted as due to a difficulty for the polymer to orient, possibly related to chain stiffness. On the other hand, it can also indicate that the polymer relaxes rapidly, even if it is oriented easily or significantly when first stretched [8].

Fig. 5 reports the $\Delta P_2/\Delta\lambda$ values for PVPh and PVME for the different compositions. In cases showing a linear behavior, only one value, corresponding to the slope for $\langle P_2\rangle$ vs. λ is reported. When linearity was not observed, the slope of the curves $\langle P_2\rangle$ vs. λ was calculated at $\lambda = 1.5$ and $\lambda = 3.0$, corresponding to low and high deformations. In these cases, two different values of $\Delta P_2/\Delta\lambda$ are therefore reported.

Within experimental error, orientation of both components of the blends appears to be comparable both at high and low draw ratios, hence the use of a single curve for both polymers. Two well-differentiated tendencies can be observed. At low draw ratios ($\lambda = 1.5$, dotted line), orientation of both PVPh and PVME components presents a maximum in orientation at PVPh42%. At high draw ratios (full line), orientation is relatively independent of concentration, within experimental error.

At low draw ratios, the higher values for PVPh42 and PVPh33% are interpreted as meaning that, for these compositions, PVPh and PVME orient easily. For $\lambda = 1.5$, only 7–8 s have elapsed between the stretching onset and the quenching of the sample, whereas for $\lambda = 3.0$ the same lapse corresponds to 15–16 s. At high λ, the supplementary time would allow the chain to reach further relaxation stages, decreasing the orientation values.

3.2. Orientation of hydroxyl forming hydrogen bonds

PVPh contains a hydroxyl moiety in the *para* position of the aromatic group which is able to form hydrogen bonds. As can be seen in Fig. 6, which presents the ν(O–H) spectral region of pure PVPh and PVPh/PVME blends, for pure PVPh, O–H segments result in two stretching absorption bands: A broad O–H vibration centred at 3370 cm^{-1}, related to ν(O–H) valence vibration of the bonded moieties, and a narrower vibration of the free O–H groups, which appears as a shoulder at 3534 cm^{-1}.

Our group previously calculated the α angle for both free and bonded O–H [6]. The two vibrations were separated using a least-square fitting method and it was supposed that orientation for both bands was the same than that of the in-plane bending of the aromatic ring vibration at 1014 cm^{-1}. A value of 65 ± 5° was obtained for the α angle of the ν(O–H) valence vibration of pure PVPh, which correspond to O–H groups involved in intrachain bonding. Although a value of 20° was proposed for the α angle of free O–H groups [22], as can be seen in Fig. 6, this vibration is of low intensity, appears as a shoulder around 3350 cm^{-1} and its α angle determination is much more

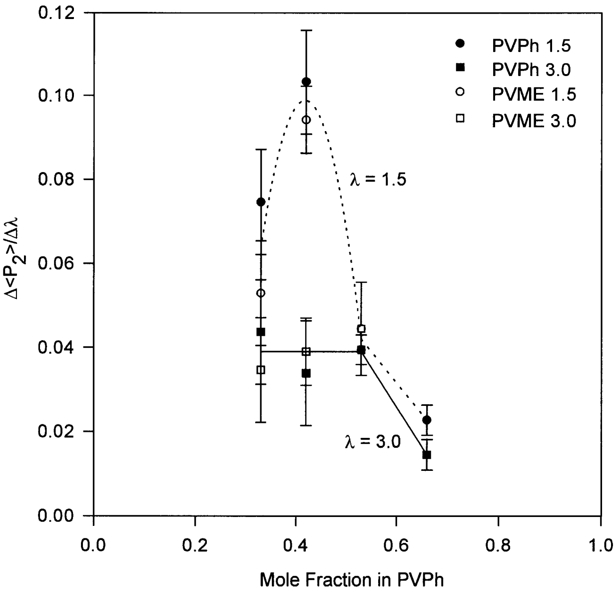

Fig. 5. Variation of $\Delta P_2/\Delta\lambda$ with composition for $\lambda = 1.5$ and 3.0 for the PVPh/PVME blends.

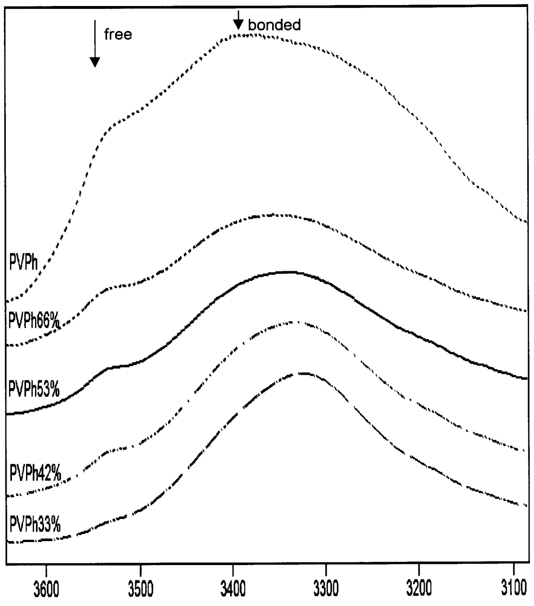

Fig. 6. Hydroxyl stretching vibration region for PVPh and PVPh/PVME blends.

uncertain. We were interested to see whether, in the blends, the same average angle between the relatively flexible O–H bond and the chain axis, α, would be observed. Changes in this angle would directly be related to changes in conformation upon interchain interactions. This was only attempted for bonded O–H groups because of the uncertainties expected for the free O–H groups. As can be seen in Fig. 6, only one vibration can be observed for bonded hydroxyls, encompassing both intra and interchain bonded O–H groups. It must be noted that these two bands are not expected to have the same absorption coefficient as the strength of the hydrogen bonds and resonance effects are different in both cases. However, to a first approximation, these can be considered to cancel out as the ratio in intensities is considered for orientation studies.

The α angles were calculated for the four compositions of PVPh/PVME assuming that bonded hydroxyls orient as much as the phenyl rings. Fig. 7 shows the plots of $\langle P_2 \rangle$ for 3021 cm^{-1} ν(C–H) valence vibration of the phenyl ring vs. $(R+1)/(R+2)$ of the ν(O–H) bonded hydroxyl vibration for the different blends. From the slope of Fig. 7 and Eq. (1), it is possible to calculate the value of the α angle. The results obtained were 71 ± 1°, 72 ± 2°, 71 ± 1° and 72 ± 2° for PVPh66%, 53, 42 and 33%, respectively, obtaining an average value of 71 ± 2°. Considering the small difference among the different values as compared to the experimental error, it can be concluded that α angle for bonded hydroxyls is not concentration dependent for the PVPh/PVME blends studied here.

The difference between the value of α for an exclusively intramolecular bonded hydroxyl (65 ± 5° as determined for pure PVPh) and that obtained for a vibration containing both intra and interchain hydrogen bonds in PVPh/PVME blends (71 ± 2°) is of 6°. It lies within the error estimated for these α angle determinated via slope variations for PVPh/PVME blends. Therefore, hydrogen bonded groups show a similar average conformation in pure PVPh and in PVME blends.

3.3. Comparison with other amorphous PVPh blends

As mentioned in Section 1, earlier orientation studies have been conducted in other PVPh blends forming intermolecular hydrogen bonds of different strength. In this section, we propose an analysis of PVPh orientation in the different amorphous systems as well as the comparison between orientation for the polymers blended with PVPh.

Fig. 8 shows the variation of $\Delta P_2/\Delta\lambda$ with composition for PVPh blended with PMMA [7] (dashed-double dotted line), PEO [8] (dashed-dotted line) and PVME (full and dashed line). For PVPh in PMMA and PEO, orientation shows a linear dependence with λ, which results in a unique value $\Delta P_2/\Delta\lambda$ for each composition. As reported earlier in this paper, in the case of PVPh/PVME, for blends richer in PVME, orientation is non-linear, and $\Delta P_2/\Delta\lambda$ was evaluated at $\lambda = 1.5$ and $\lambda = 3.0$. For PVPh in PMMA, in PEO and in PVME at $\lambda = 3.0$, orientation is not markedly affected by composition in the middle composition range, differences in orientation usually being within experimental error. At high PMMA compositions, a marked increase in orientation of PVPh was observed. Unfortunately, orientation data in this composition range was not available for PVME and PEO blends because of the vicinity of blend T_g vs. room temperature, which made quenching ineffective. In the case of PEO blends, crystallization also appeared at high PEO concentrations, which was an additional reason for not investigating such compositions.

The lower values for PVPh in PEO blends can be partially attributed to the fact that the T_g of PEO is the lowest

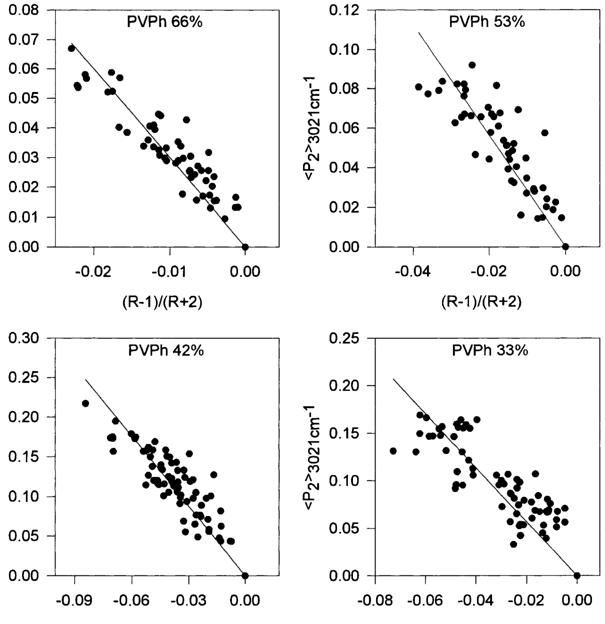

Fig. 7. Determination of the transition moment angle of the hydroxyl stretching vibration for the different PVPh/PVME blends.

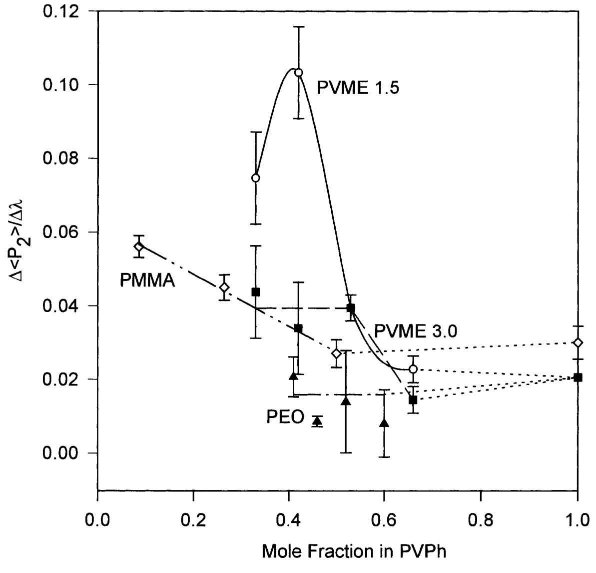

Fig. 8. Variation of $\Delta P_2/\Delta\lambda$ with composition for PVPh in different blends.

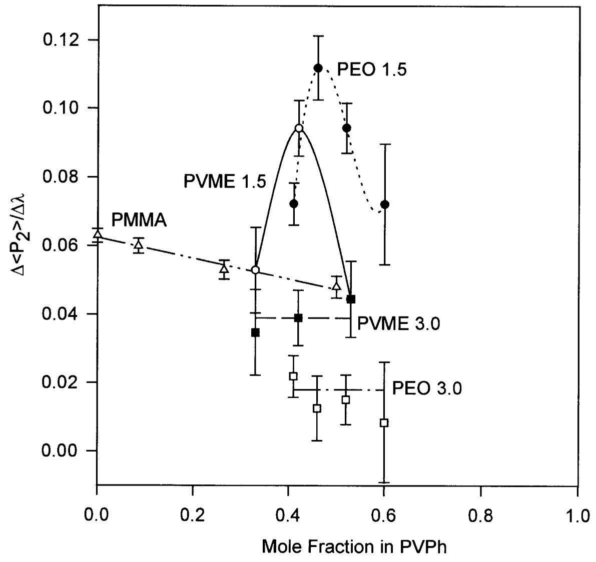

Fig. 9. Variation of $\Delta P_2/\Delta\lambda$ with composition for PMMA, PEO and PVME in blends with PVPh.

(−60°C) [8], compared to PMMA (94°C) [7] and PVME (−22°C). In the PMMA system, the glass transition temperature is well above room temperature, so quenching will be most successful, followed by PVME blends and PEO blends, for which blend temperature is closer to room temperature and quenching efficiency reduced [8]. Dynamical orientation measurement methods, such as polarization modulation infrared linear dichroism (PM-IRLD), would be necessary to determine whether the lower orientation observed for PVPh is due solely to relaxation effects or not.

Fig. 9 shows $\Delta P_2/\Delta\lambda$ with composition for PMMA, PEO and PVME in amorphous PVPh blends. For PMMA there is a linear behavior with draw ratio, resulting in one $\Delta P_2/\Delta\lambda$ value for each composition. However, for both PEO and PVME a different behavior can be observed at low ($\lambda = 1.5$) and high ($\lambda = 3.0$) deformation ratios. At low draw ratios, both PEO and PVME present a maximum of orientation near a 1:1 mole ratio. At high ratios, PEO and PVME orientations are independent of deformation, within experimental error, which is consistent with the previous analysis: At higher deformation values, the elapsed time is higher, so these polymers experience further relaxation stages, which reduce final orientation values.

3.4. Orientation maximum in blends with hydrogen bonds

A feature worthy of discussion in hydrogen bonding blends is the occurrence of a maximum in orientation near a 1:1 mole ratio for two amorphous PVPh blends, PVPh/PEO and PVPh/PVME. The difference between orientation for PVPh/PMMA blends and for PVPh/PEO and PVPh/PVME systems, which appear in Figs. 8 and 9, is noteworthy. For PMMA blends, we observe a concentration-dependent behavior and a single value for $\Delta P_2/\Delta\lambda$ for each composition. For the other two blends, there is a maximum in orientation for one or both components of the blends at low draw ratios and the behavior is almost concentration independent at high draw ratios.

The difference in the trends at low draw ratios can be explained in terms of hydrogen bond strength. PMMA forms weak intermolecular hydrogen bonds with PVPh. Hydrogen bonds may slow down relaxation of the flexible chain (PMMA, PEO or PVME), but in the case of PVPh/PMMA, due to their weakness in comparison to intramolecular hydrogen bonds, these interactions may only allow to maintain an intermediate orientation between that of the pure polymers. This could explain the concentration dependence. The same behavior has been reported for blends forming weak intermolecular bonds, as for PVC/PMPPL blends [3]. Moreover, results of PS-VP/PS-PMAA blends by Bazuin et al. [5] can be subjected to the same interpretation.

In PVPh/PEO and PVPh/PVME blends, intermolecular hydrogen bonds are stronger than intramolecular hydrogen bonds. Near a 1:1 composition, the number of units apt to form intermolecular hydrogen bonds is maximum (50% hydroxyl units from PVPh and 50% ether units from PVME). As these interactions are strong, orientation can also attain a maximum at this concentration since relaxation will be minimal.

Furthermore, Lezcano et al. [17] have shown that the interaction parameter for PVPh/PVME presents a maximum at equimolar compositions. The relation between stronger interactions and higher orientation has already been advanced by Jasse et al. [1]. At low draw ratios, the stronger interactions would hinder relaxation, as they increment the friction coefficient.

Consequently, in the case of blends forming strong hydrogen bonds, orientation is proposed to depend on interaction fluctuations in strength or number. Either Wu [23], using a rheological approach, or Jasse et al. [1], based in PS/PPO orientation experiments, proposed that an increase in interactions would increase the friction coefficient, therefore modifying the relaxation conditions. This explanation can be applied to the PVPh/PEO and PVPh/PVME orientation results. At compositions where these blends showed a maximum in interactions, friction coefficients would be higher and, as a consequence, relaxation times would increase, yielding higher final orientation values.

It is noteworthy that in PVPh blends, at low draw ratios, PEO $\langle P_2 \rangle$ orientation values are consistently higher that those for PVME at low deformations. This could be due to PVPh/PEO intermolecular hydrogen bonds being stronger those for PVPh/PVME, as was shown by other groups using FTIR spectroscopy [9,11] and calorimetry [11]. It is important to point out than, when blended in system with weak interactions (dipole–dipole), PEO and PVME have exhibited no orientation (PMMA/PEO) [2] or very slight orientation (PVME/PS) [14].

3.5. Comparison with PS/PVME blends

The PS/PVME is a system structurally very close to the blend studied here, the main difference being the hydroxyl moiety in the *para* position of PVPh, which allows it to form hydrogen bonds. Therefore, whereas in PVPh/PVME miscibility is related to strong hydrogen bonding interactions, in PS/PVME blends, the interactions between both polymers are dipole–dipole [24], thus weaker than hydrogen bonds. In addition, hydrogen bonds are responsible for the higher glass transition temperature of PVPh (172°C) when compared to PS (100°C). Therefore, for the same PVME composition, PVPh/PVME blends would have higher T_g values than PS/PVME blends.

Orientation of amorphous PS/PVME blends have been extensively studied [12–16] using birefringence, FTIR and polarized modulated infrared spectroscopy, showing that orientation is composition dependent for both polymers. Moreover, for PS/PVME blends, the χ interaction parameter is strongly composition dependent [25,26]. It must however be noted that the molecular weights studied for PS/PVPME are different from those of the PVPh/PVME reported in the present study. Care must therefore be taken when comparing quantitatively the two systems.

Fig. 10 shows the initial orientation slopes ($\Delta P_2/\Delta\lambda$) for the amorphous PS/PVME and PVPh/PVME systems. Data for the PS/PVME system were calculated from graphs appearing in the work of Abtal and Prud'homme [14]. It should be noted that PVME orientation in PS/PVME blends is reported as the contribution of PVME to the total birefringence ($\Delta o_{\mathrm{PVME}}\langle P_2\rangle$), hence, the product of the intrinsic birefringence (Δo_{PVME}) and the second moment of the orientation function ($\langle P_2\rangle$) for this component [14]. Fig. 11 reports their χ interaction parameters, as taken from the work of Han et al. [25] and of Lezcano et al. [17] previously reported in the literature, for the PS/PVME and PVPh/PVME systems, respectively. In both cases the maximum in orientation (64 mol% in PVME for PS/PVME blend and 58 mol% in PVME for PVPh/PVME) is at a concentration value close to that where the minimum in χ is observed (64 mol% in PVME for PS/PVME blend and 67 mol% in PVME for PVPh/PVME). As the interaction parameter becomes more negative, interactions are stronger, supporting the hypothesis that the maximum in orientation would be related to a maximum in interactions. As mentioned above, an increase in interactions is related to an increase in the friction coefficient [1,23], hindering relaxation.

In spite of the fact that, for PS/PVME blends, both polymers show a maximum in orientation, orientation values for both components are very different, PS being considerably more oriented that PVME. This may be partially related to the molecular weights used in these studies, for which PS is much higher (254,000–942,000 g mol^{-1}) and PVME much lower (44,000–90,000 g mol^{-1}), whereas the reverse situation was used in the present work. Nevertheless, Pellerin et al. saw no evidence of cooperative relaxation when investigating the PS/PVME blend using a dynamic technique (PM-IRLD) [16]. In PVPh/PVME, both components have similar orientation values, implying a cooperative relaxation. We believe that this point is worthy of specific attention.

3.6. Orientation cooperativity for blends with hydrogen bonds

It has been proposed in several articles in the literature that, for systems containing hydrogen bonds, both polymers relax jointly. Saito et al. [27] concluded that cooperativity in relaxation occurred at the molecular or segmental level for both components in poly(methyl methacrylate)–poly(vinylidene fluoride) and poly(methyl methacrylate)–poly(vinylidene fluoride-co-trifluoroethylene) systems, which form weak hydrogen bonds. The authors suggest that, in general,

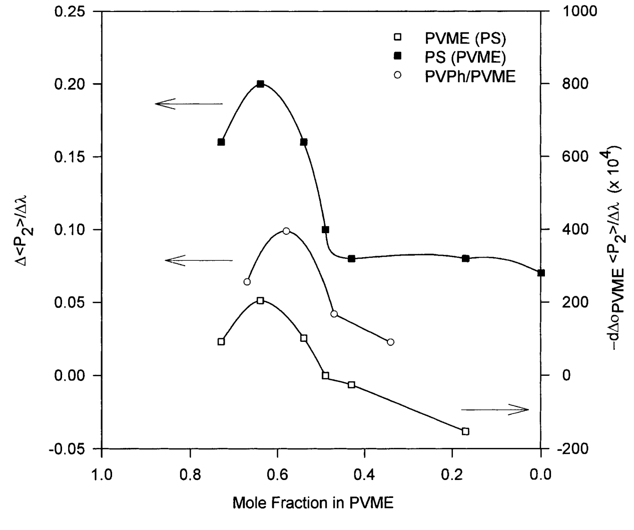

Fig. 10. Variation of $\Delta P_2/\Delta\lambda$ with composition for PS/PVME [14] and PVPh/PVME blends.

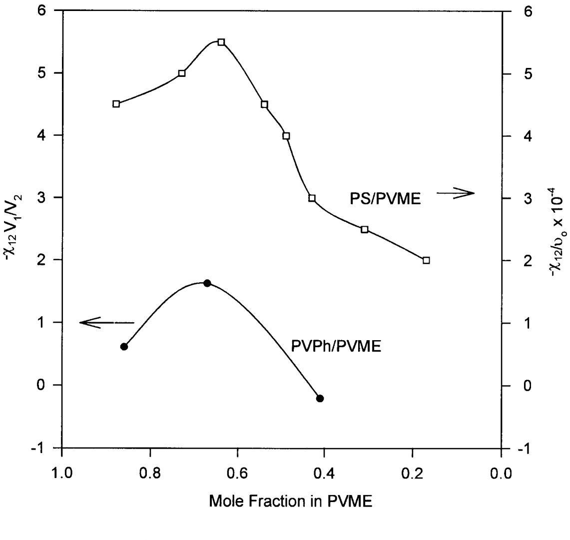

Fig. 11. Variation of the χ interaction parameter with composition for PS/PVME [25] and PVPh/PVME [17] blends.

hydrogen bond would favor cooperative relaxation, hydrogen bonds hindering relaxation.

In the case of poly(vinyl chloride)–poly(α-methyl-α-*n*-propyl-β-propilactone) (PVC/PMPPL), Chabot et al. [3] showed there is a decrease in PMPPL orientation upon addition of PVC, which is also the case when adding PMPPL to pure PVC, at least for the *gauche* conformers. Moreover, for the 30:70 PCL/PMPPL blend, the sole composition reported for which the blend is amorphous, similar behavior is observed for *gauche* PVC segments and for PMPPL orientation, an observation that also supports the idea of a cooperative relaxation for hydrogen bond containing blends.

Bazuin et al. [5] reported that, for up to a 12% copolymer content, hydrogen bonds between carboxylic groups did not influence orientation of PS-VP/PS-PMAA, as mentioned in Section 1. This may be due to the fact that, in general, alkyl carboxylic acids hydrogen bonds are weaker than phenolic, as showed by Ruokolainen et al. [28] for blends of poly(4-vinylpyridine) with different classes of hydrogen-bonding surfactants. On the other hand, Bazuin et al. reported that sulfonic groups of poly(styrene-*co*-styrene sulfonic acid) did induce a substantial orientation increase as compared to poly(styrene) [5]. As pure PS-MAA has the same orientation that pure PS [5], weak hydrogen bonds may not enhance orientation, but simply favor cooperative relaxation. Therefore, orientation of PS-VP/PS-PMAA blends is expected to be the same as that of the pure components, as in fact was the case.

Although, using quenched samples, cooperativity assessment is not as straightforward as with dynamical measurements, several features that can be related to cooperativity arise from the comparison of PVPh/PVME blend with other PVPh blends and with PS/PVME and PMMA/PEO blends. Firstly, for PVPh based blends, orientation values are in the same orientation range for both components of the hydrogen bond forming blend, with the exception of PVPh orientation in PVPh/PEO blends. The difference for this system can be explained as the M_w of the PVPh used in PEO blends was of only 5200 g mol^{-1}, whereas the molecular weigh between entanglements, M_e, for this polymer is estimated to be around 23,000 g mol^{-1} [29]. The fact that the molecular weigh of the polymer is well under the M_e value suggests that PVPh would not be entangled with itself, so the orientation obtained through deformation would relax very fast.

Secondly, as mentioned previously, no orientation was observed for PEO in blends with PMMA [2], and no [12,13] or very limited [14] orientation was reported in the case of PVME in blends with PS. In both cases, the other component of the blends (PMMA and PS, respectively) did orient. The mentioned studies suggested that the different behavior for both components in the blends was related to an absence of coupling during deformation and relaxation for both components. As signaled in the precedent section, Pellerin et al. [16], showed, using PM-IRLD to record relaxation of PS/PVME blends, that no relaxation coupling could be clearly observed between the two polymers, the relaxation rate of PVME being always faster than that of PS. On the other hand, as was observed in Figs. 8 and 9, in the case of PEO and PVME blended with PVPh, both PEO and PVME retain a significant orientation after quenching. This suggests that deformation and/or relaxation is cooperative in the PVPh/PEO and PVPh/PVME blends.

4. Conclusions

PVPh/PVME blends show significantly higher values of orientation for both components near equimolar composition. This result is related to an interaction maximum, which should increase the friction coefficient and hinder relaxation. Both components have a similar behavior, within experimental error, suggesting cooperative deformation and relaxation processes. Higher orientation slopes at low draw ratios when compared to high deformation values suggest that experimental data at low and high deformation ratios may have been subjected to different relaxation stages. This is due to the low T_g values of the blends, near the room temperature, which reduce quenching efficiency and favor relaxation.

It was found that the α angle of bonded O–H valence vibration is not concentration dependent for PVPh/PVME, which indicates that no major conformational change takes place when forming interchain vs. intrachain hydrogen bonds.

From the comparison with PVPh/PMMA and PVPh/PEO blends, which form hydrogen bonds, it is suggested that this type of interaction hinders the relaxation process, favoring cooperativity. Moreover, it is suggested that orientation for systems containing weak interchain hydrogen bonds would lie between orientation values of the pure polymers. Both systems containing strong intermolecular hydrogen bonds, PVPh/PEO and PVPh/PVME, showed a maximum of orientation. This has been related to an increase of the interaction strength, which would hinder relaxation and increase the friction coefficient.

When PVPh/PVME results are compared with those obtained for PS/PVME blends, a structurally similar system but lacking hydrogen bonds studied by other research groups [14,16], it was found that both blends manifest a maximum in orientation, which was related to a maximum in interactions. However, in the PVPh/PVME system, both components orient similarly, whereas in PS/PVME, PS orients much more that PVME. This difference can be explained in terms of interactions strength: Whereas the PVPh/PVME system forms hydrogen bonds of medium strength, the PS/PVME system experiences weaker van der Waals forces (dipole–dipole).

Molecular modeling simulations are currently under way in our laboratory in order to further investigate the role of hydrogen bonds in orientation and relaxation processes.

Acknowledgements

The authors thank R. Plesu of the CERSIM for mass determination of PVME and S. Bonenfant and S. Groleau, also of the CERSIM, for technical support in FTIR measurements. This research was supported by the NSERC (National Science and Engineering Council of Canada), and by the FCAR (Fonds pour la Formation des Chercheurs et l'Aide à la Recherche). P. Gestoso also acknowledges the support of the scholarships from the Ministère de l'Education du Québec and from Université Laval.

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