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Polymer 40 (1999) 1969–1978

polymer

Blends of polycaprolactone with polyvinylalcohol: a DSC, optical microscopy and solid state NMR study

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Received 5 March 1998; accepted 17 April 1998

Abstract

Blend films of polycaprolactone (PCL) and polyvinylalcohol (PVAl) have been obtained by evaporation of a solution of both components in hexafluoroisopropanol. The miscibility of the polymers in the amorphous part of the blend has been studied by conventional methods (optical microscopy, DSC and FTIR) and by solid state NMR. Phase separation is observed in the melt. The absence of any lowering of Tm and the presence of one low temperature *Tg* near that of pure PCL support the hypothesis of phase separation in the amorphous part of the blend. However, various experimental data suggest the presence of some type of physical interactions between components. These data are: the important decrease of PCL crystallinity in the blend, the morphology of PCL spherulites after crystallization at 45°C and the absence upon annealing the blend at 50°C, of any rearrangement of PCL crystallites into spherulites as observed in pure PCL. The measurement of proton spin-lattice relaxation time T_1 by solid state NMR using cross polarization has shown that the components are compatible at the scale of 60–90 nm and are thus very finely dispersed into each other. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Nuclear magnetic resonance; Polycaprolactone; Polymer blends

1. Introduction

Blends of two semi-crystalline polymers have been seldom investigated. Two crystalline phases are generally observed since polymer co-crystallization is uncommon. The problems to be solved concern the number and composition of amorphous phases. Various possibilities exist:

- The polymers are miscible in the amorphous part of the blend which forms one unique amorphous phase where the two crystalline structures are dispersed.
- The polymers are completely immiscible in the amorphous part of the polymer. The film is then constituted of two semi-crystalline phases of the pure components. The degree of dispersion of the components depends on the method of preparation of the blend. If the dispersion is very fine, the spherulite of the major component can engulf the minor component during growth.
- The polymers are partly miscible in the amorphous part. The blend then generally contains two semi-crystalline phases, each of them being richer in one of the components which crystallizes partly and is the major constituent of the corresponding amorphous phase.

The morphology and scale of compatibility of the blends as defined by Utracki[1] are determined by the method of preparation of the film. In the case of blends prepared by evaporation of a solution of both components as in the present case, this morphology depends on thermodynamic and kinetic parameters. The thermodynamic parameters are fixed by the ternary phase diagram of the components. Kinetic parameters are related to the rate of phase separation. This one depends on the rate of evaporation of the solvent and on the viscosity of the medium which can freeze a given morphology at a given time. Heating such films above the higher melting point for a short time does not necessarily induce miscibility even if it is thermodynamically allowed. Indeed, homogenization of the melt by diffusion can be limited by the dimensions of the phases resulting from solvent evaporation. The blend studied in the present work was chosen for two reasons. Firstly, PCL is an aliphatic polyester aerobically degraded by a large number of microorganisms in various microbiological environments. Secondly, PVAl is often blended with PCL and other biodegradable polymers to optimize the hydrophobic–hydrophilic properties of the final material. The results concerning the assimilation of PVAl/PCL blends by microorganisms has been published previously[2]. This study

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PII: S0032-3861(98)00253-5

required an extensive knowledge of the compatibility of the blend components which is the topic of the present paper.

2. Experimental

2.1. Polymers

Polycaprolactone CAPA 640 ($M_n = 37.000$) was kindly supplied by Solvay-Interox. Polyvinylalcohol (Mowiol 4-98) was obtained from Hoechst. Its molecular weight is 23.000 and its percent hydrolysis is 98 ± 0.4 mol%. All films were obtained by dissolving predetermined weights of each polymer in hexafluoroisopropanol, mixing the obtained solutions for 24 h and evaporating the final solutions at room temperature in Teflon dishes for 24 h. The films were dried in vacuo for 5 days at room temperature and 4 days at 50°C. The concentration and quantity of solution were adjusted to obtain films 50–70 μm thick. In the following sections, the blends are characterized by their composition given in weight percent. The first and second number, respectively, refer to PVAl and PCL. The melting point, weight percent crystallinity and glass transition temperature of the films were measured using a Perkin-Elmer DSC 7 apparatus. The melting point was determined at the maximum of the melting endotherms obtained at a scanning rate of 20°C/min. The weight percent crystallinity was calculated assuming values of 136 and 152 J/g for the 100% crystalline PCL and PVAl samples. Only approximate values could be obtained because the solvent is difficult to eliminate.

2.2. NMR measurements

The NMR measurements were performed using a MSL 400 Bruker spectrometer operating respectively at 400.13 and 100.61 MHz for ^{1}H and ^{13}C.The proton relaxation times T_1 have been measured directly and through ^{13}C using dipolar decoupling (DD), cross-polarization (CP) and magic angle spinning (MAS).

The direct measurement of T_1 was performed by the classical inversion-recovery method. A radio frequency field B1 was applied during a pulse time of 1.4 μs in order to shift the magnetization by 180°. Decay was observed after 25 delay times τ ranging between 15 and 10^{-3}s for PVAl and between 10 and 10^{-5}s for PCL. For the blends, 33 decay times ranging between 15 and 10^{-5}s were used. After time τ, magnetization was shifted by 90° by applying B_1 during 0.7 μs. After 2 μs delay, decay of the transverse magnetization (Free Induction Decay) (FID) was measured as a function of time during 819 ms. The Fourier Transform of the signal gives the NMR magnetization intensity as a function of frequencies. This pulse sequence was repeated after a time t_r (repetition time) of 157 and 15 s respectively, for PVAl, PCL and the 50/50 blend. The number of accumulation was 32, 56 and 88, respectively for PVAl, PCL and the 50/50 blend. The base line of the spectra was manually corrected for each τ value. The intensities were measured at the maximum of the broad bands. The initial intensity of the signal I_0 was obtained from the intensities corresponding to the longest τ values. Graphs of ln $(I_0 - I)$ as a function of τ gave the relaxation time T_1. The proton spectra were recorded for the longer τ values. The protons are then completely relaxed and magnetization along B_0 is maximum.

^{13}C solid state NMR was performed classically using cross polarization, dipolar decoupling and magic angle spinning at a frequency of 3.8 kHz. Cross polarization allows the measurement of proton T_1 by the way of resolved ^{13}C resonances. These T_1 values were determined by the inversion recovery method. A radio frequency field B_1 was applied during a pulse time of 10 μs in order to shift the magetization by 180°. Relaxation was allowed during various times τ. Ten τ values lying between 15 and 0.025 s were used for PVAl and PCL, while 29 values ranging from 25 to 0.01 s were necessary for the blends. The resulting proton magnetizations after time τ were measured using a cross polarization sequence. This involves shifting of the proton magnetization by 90° using a radio frequency field B_{1H} during 5 μs, dephasing it by 90° to lock the spin in the rotatory frame during the time of acquisition and transferring ^{1}H magnetization to ^{13}C under Hartmann–Hahn conditions during a contact time t_{CT}. This contact time was adjusted to obtain a maximum magnetization of ^{13}C. The details of the t_{CT} determination are given in Section 3.8. After a delay time of 20 μs, the ^{13}C magnetization decay was recorded by FID during an acquisition time of 50 ms under proton decoupling conditions. The repetition time was 7 s for PCL and 25 s for PVAl and the blends. The number of accumulated sequences was equal to 260 for all samples with the exception of the 80/20 blend for which it was 360. The base lines were manually corrected and the intensity values measured at the maximum of the peaks. The initial magnetization I_0 was determined for the longer τ values. The T_1 values were obtained by exponential regression using the Bruker SIMFIT program. The ^{13}C spectra were obtained from the longer τ values.

3. Results and discussion

Miscibility of the film components in the melt will be first considered. Thereafter, attention will be paid to the study of the scale of compatibility of the components at room temperature and more particularly to their miscibility in the amorphous phase. Various traditional methods will be used. Their limitations will lead to an investigation by solid state NMR. The definitions of miscibility, partial miscibility, and non-miscibility are those of Paul and Barlow[3].

3.1. Miscibility in the melt

This can be determined by direct observation of the

Table 1
Glass transition of PVAl, PCL and their blends

Composition PVAl/PCL	$Tg_{\text{calc.}}$ (°C)	$Tg_{\text{obs.}}$ (°C)	
		PVAl	PCL
PVAl	–	81	–
80/20	19.1	NO[a]	−61
50/50	−13.5	NO	−55
20/80	−33.3	NO	−62
PCL	–	–	−60

[a] NO = non observed.

primary film after heating above the melting temperature of the highest melting polymer. The molten film was kept for 2 min at 250°C and then rapidly quenched in liquid nitrogen. The molten state is then frozen and the number of the phases can be determined. In these conditions, macroscopic phase separation can be observed with the naked eye or with the polarizing microscope. It can be concluded that the blend films prepared by solvent evaporation in the conditions used in the present work and thermally treated as described here are either immiscible or partly miscible in the melt, each phase containing then one of the polymers as the main component. These considerations mean that the study of the morphology of the primary films used in this work have to be performed in the absence of any thermal treatment involving melting.

3.2. Miscibility of the components in the amorphous part of the film (measurement of Tg)

The most significative parameter to be measured for that purpose is the glass transition temperature. Indeed, it is well established[1] that in blends compatible at the scale of 50–100 carbon atoms in the main chain (5–10 nm), a unique *Tg* is observed which obeys Fox relation[4]. It is also well known that *Tg* is difficult to measure for semi-crystalline polymers. Indeed, the amorphous rigid interfacial region situated between the lamellar crystals and the amorphous phase does not transform into a mobile amorphous liquid at *Tg* and is not observable by DSC in the usual conditions used for the measurement of this parameter. Since this interfacial region often contains a high fraction of the total amorphous region, polymers are usually quenched from the melt to a temperature situated well below *Tg* to decrease its importance. It has been shown above that this cannot be done in this work. Therefore, the primary films have been heated in the usual conditions (20°C/min from −100°C to 200°C) and investigated directly. The obtained results are given in Table 1 together with the values calculated with Fox equation which is valid in the case of miscibility in the amorphous phase. For the three blends, a low temperature *Tg* very similar to that of pure PCL and thus very far from Fox values have been observed. It can be concluded that the blend films contain one phase of pure or almost pure PCL. The other phase is thus either pure PVAl or a blend containing PVAl as the main component. The *Tg* of the second phase would lie in the range of PCL melting and could not be observed. It can, nevertheless, be concluded that PVAl and PCL are not miscible in the amorphous part of the blend. They are either immiscible or partly miscible and are incompatible at the scale of 5–10 nm. Determination of the scale of compatibility of both phases is thus full of interest.

3.3. Direct identification of hydrogen bonds

This can often be done by IR spectroscopy. PVAl being strongly auto-associated, observation of H-bonds between PVAl and PCL in the OH region is difficult and, as expected, no change could be detected. The carbonyl absorption of PCL[5] is composed of a maximum situated at 1724 cm^{-1} associated with the crystalline part of the polymer and of a shoulder at 1731 cm^{-1} corresponding to the amorphous fraction. No change was observed in the position of the maximum indicating that interpolymer H-bonds, if present, are quite weak.

3.4. Melting and crystallization behavior

The melting temperatures measured at the maximum of the melting endotherm are given in Table 2. The T_m value of PVAl does not depend on blend composition. For PCL, some complicated dependence is observed; it is probably due to the broad endotherm resulting from elimination of residual traces of solvent which are expelled in the same temperature range as melting. These observations mean that either the components are not miscible in the melt at the melting point as shown above or that the interaction

Table 2
Melting temperature, melting enthalpy and crystallinity index of PVAl and their blends

Composition PVAl/PCL	PVAl			PCL		
	T_m (°C)	ΔH_f (J/g$_{\text{PVAl}}$)	Crystallinity (%)	T_m (°C)	ΔH_f (J/g$_{\text{PCL}}$)	Crystallinity (%)
100/0	219	73.7	48.4	–	–	–
80/20	220	87.8	57.7	65.4/59.0*	29.6	21.8
50/50	220	83.1	54.6	67.0	59.7	44.0
20/80	220	77.5	50.9	64.9	92.8	68.4
0/100	–	–	–	69.7	89.8	66.2

* Double endotherm.

parameter χ has a very small value. The variation of ΔH_m and hence of the crystallinity index is more significative. Let us remember that crystallization in the primary film does not result from a thermal treatment during cooling of the melt, but from solvent evaporation at room temperature. The crystallinity index is rather constant for PVAl, but for PCL, it strongly decreases with decreasing PCL content (Table 2). This behavior is generally assigned to interaction between components during crystallization. In miscible blends of one semi-crystalline polymer such as PVAl and one amorphous polymer such as polyacrylic acid (PAA)[6] complete suppression of the crystallinity was even observed for blends containing more than 50% PAA. In the present case, we know from the preceding sections that PVAL and PCL are not miscible. We can nevertheless conclude that there are some interactions between PCL and PVAl when PCL crystallizes while PVAl, which probably crystallizes first, is free of these interactions.

3.5. Annealing of the films at 50°C

When a primary film of pure PCL dried in vacuo at room temperature for 5 days is annealed in vacuo at 50°C for 4 days, reorganization of the small crystallites into spherulites of about 30 μm in diameter occurs. Such reorganization is not observed in blends treated in the same conditions indicating that some type of interactions between PVAl and PCL inhibits crystallite reorganization into larger entities. Let us remember that PVAl is crystalline and glassy at 50°C.

3.6. Kinetics of PCL crystallization in films obtained by evaporation at 70°C

In this case, hexafluoroisopropanol solutions are concentrated at room temperature and then warmed up to 70°C before any crystallization and phase separation occur. Vaporization of the residual solvent is performed at this temperature which lies above the melting range of PCL but below the glass transition and melting of PVAl. Spherulite growth rate for PCL was measured at 45°C for pure PCL and the three blends. The results are given in Table 3. The growth rate is constant for each sample indicating a constant concentration of the crystallizing component at the growing end of the lamellae. However, it decreases with decreasing PCL content being roughly proportional to it. Concentration dependence of spherulite growth rate in miscible melts is well known to be very complicated[7,8]. It involves the preexponential factor, but also the transport and nucleation terms. This dependence varies from one system to another. However, a very strong decay of the growth rate with diluent polymer concentration is usually reported in the literature. As an example[9], on passing from pure polyethylene oxide to blends containing 30% PMMA the growth rate decays from 153 to 6.1 μm/min. at 48°C. The weak variation with composition observed for PVAl/PCL blends (2.2 to 1.6 μm/min. at 45°C in the same composition range) is a complementary argument to the previously stated proposal that the components are not miscible in all proportions. More interesting is the morphology of the spherulites. In pure PCL, spherulites with Maltese cross and polygonal edges are observed (Fig. 1) while in the blends ring banded spherulites limited by hyperbole branches are growing. Ring banded spherulites are often assigned to growth under constraints[10]. The formation of spherulites limited by hyperbole branches is attributed to time dependent primary nucleation while the linear edges of pure PCL suggest that all spherulites are nucleated simultaneously[11]. The observations of this section can also be assigned to some kind of interaction between the non miscible components of the blend. The second part of this paper will be concerned with the measurement of the scale of compatibility of the blend and the identification of the nature of the so far observed interactions between the components.

Table 3
Radial growth rate G of PCL spherulites at 45°C as a function of blend composition

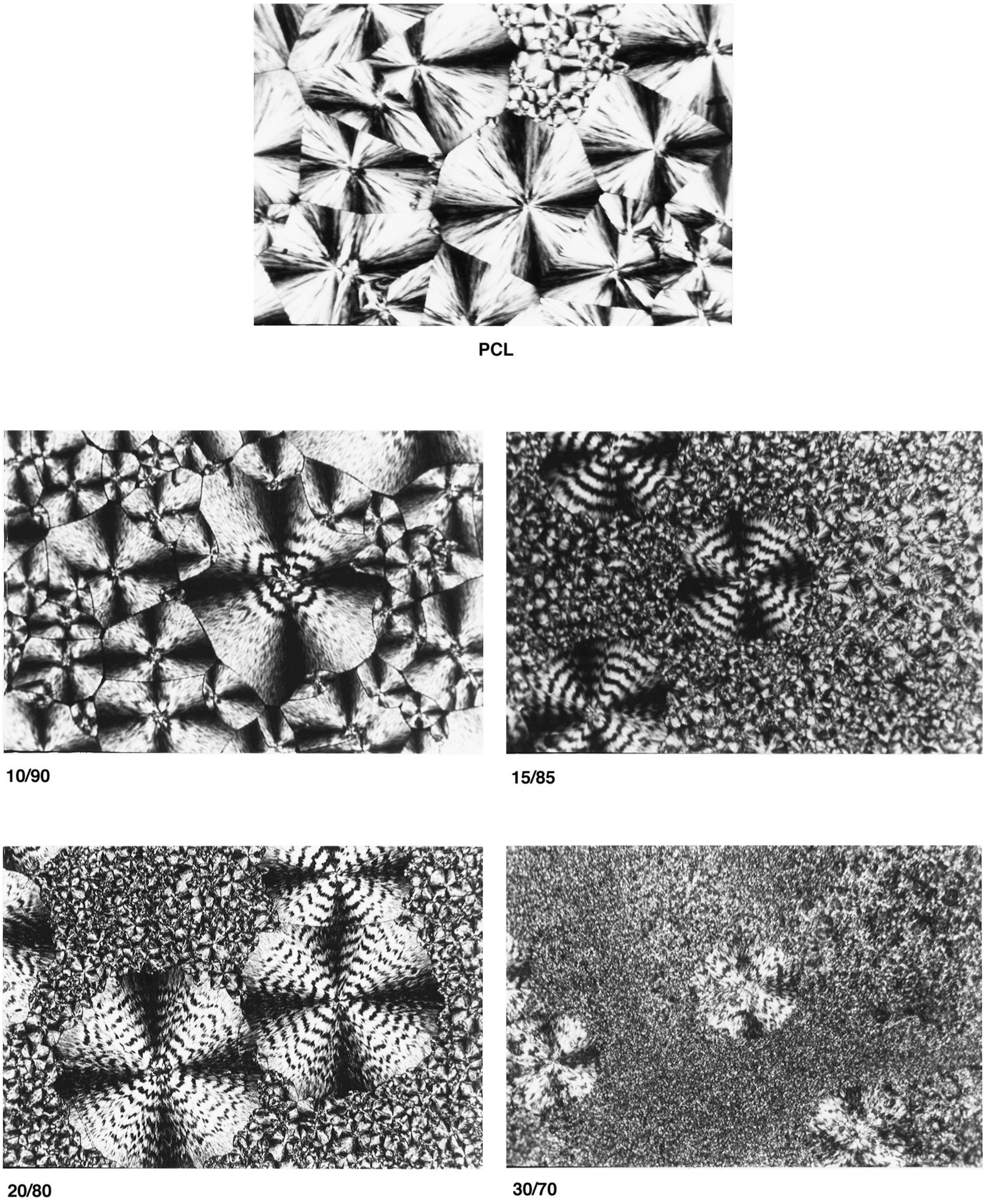
Composition PVAl/PCL	G(μm/min)
0/100	2.2
10/90	2.1
15/85	1.7
20/80	1.8
30/70	1.6

3.7. Direct measurement of the proton spin lattice relaxation time T_1

Direct observation of proton resonance gives broad band unresolved spectra owing to $^1H-^1H$ dipolar interactions. The spectra of PVAl, PCL and the 50/50 blend are given in Fig. 2. The observed band is clearly the superposition of two contributions due to the rigid and mobile parts of the sample. The broader contribution (I) is due to the rigid crystalline and glassy fractions while the narrower (II) corresponds to the more mobile amorphous rubbery fraction. The contribution of the mobile part is more important in PCL since the amorphous part of this polymer is rubbery at room temperature, while PVAl is glassy. Monoexponential decay is obtained in all cases. The relaxation time T_1 is 3.2, 0.9 and 2.1 s for pure PVAl, pure PCL and the 50/50 blend. It indicates that at the scale of T_1, spin diffusion is sufficiently efficient to homogenize proton magnetization in the crystalline and amorphous phase on one hand and blend domains on the other hand. ^{13}C NMR using cross-polarization will allow confirmation of this result by measurement of T_1 on resolved resonances corresponding to different carbons of PCL or PVAl.

3.8. Determination of the contact time in cross-polarization

In the conventional CP process under Hartmann–Hahn conditions, ^1H and ^{13}C spin systems are spin-locked in the


PCL

10/90

15/85

20/80

30/70

Fig. 1. Optical micrographs obtained at room temperature of PCL and PCL rich blend films after crystallization at 45°C of films obtained by evaporation of hexafluoroisopanol solutions at 70°C.

rotating frames and thermally contact each other, thus exchanging their energies. The respective spin systems also exchange energies with the surrounding thermal reservoir, the so-called lattice. According to the simple theory of the CP process[12] ^{13}C magnetization, $M_C(t)$, is expressed as a function of the contact time t as follows:

$$M_C(t) = (M_e/T_{CH})(1/T^*_{1\rho C} - 1/T_{1\rho H})^{-1}$$

$$[\exp(-t/T_{1\rho H}) - \exp(-t/T^*_{1\rho C})], \tag{1}$$

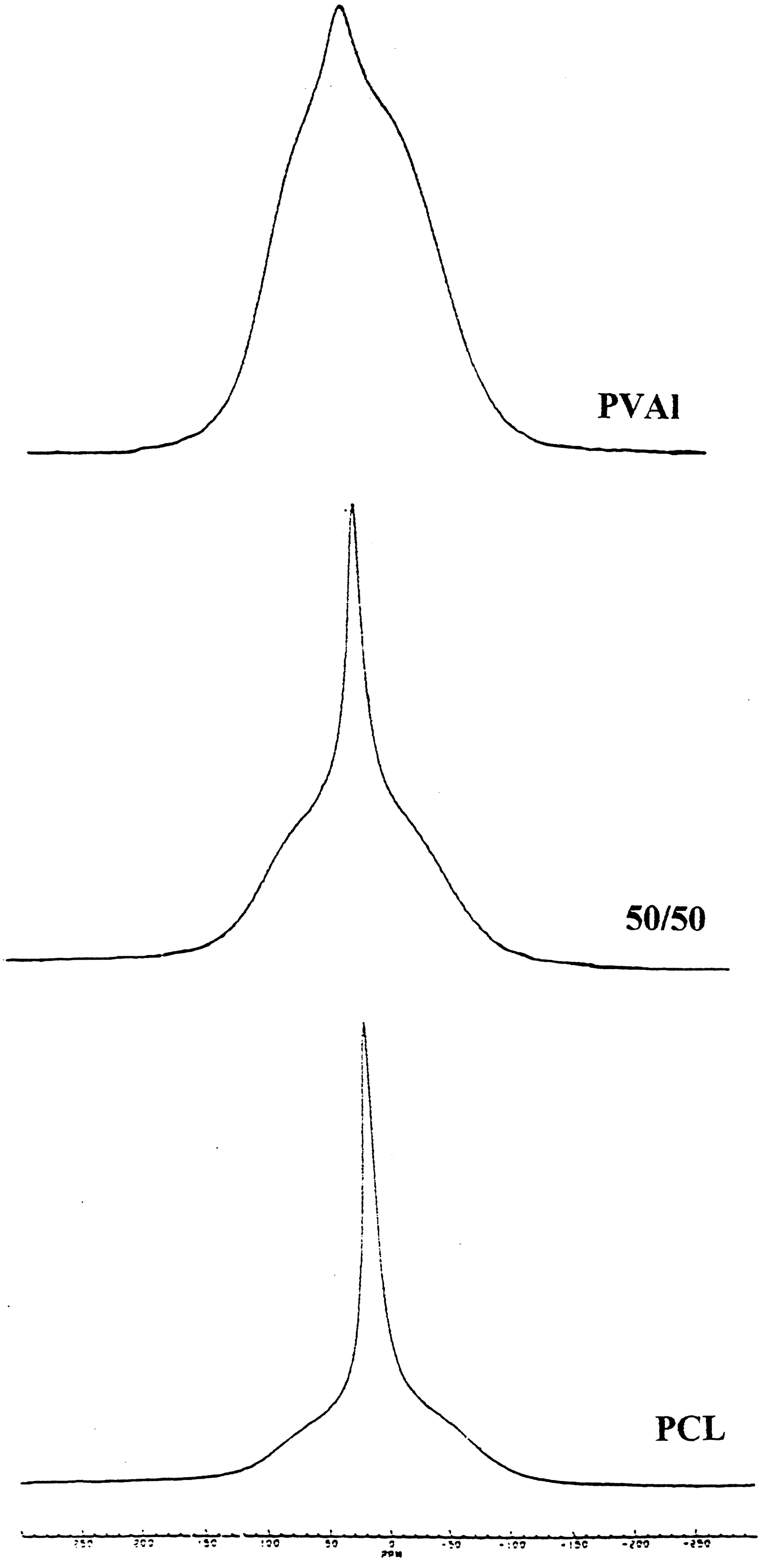


Fig. 2. Broad band ^{1}H NMR spectra of PVAl, PCL and the 50/50 blend.

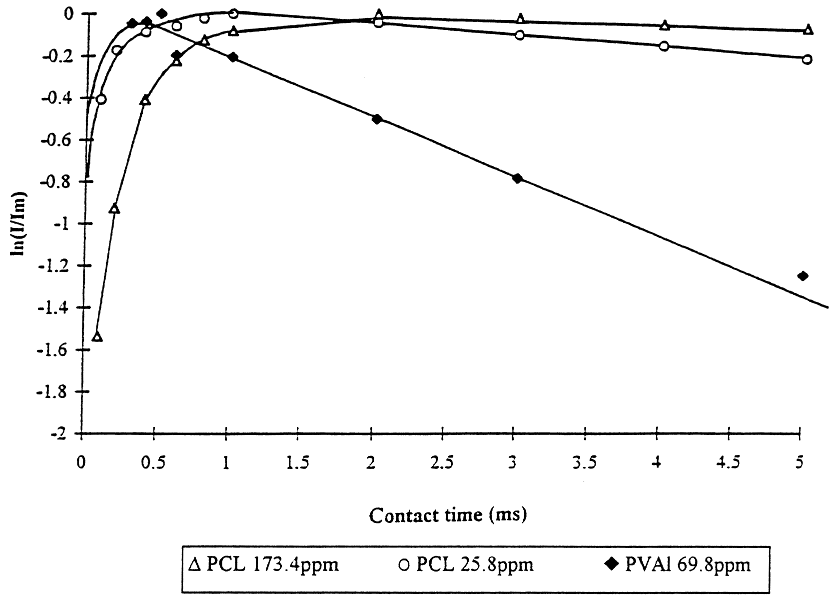


Fig. 3. Intensity of the PCL resonances at 173.4 and 25.8 ppm and of the PVAl resonance at 69.8 ppm as a function of the contact time.

where

$$1/T^*_{1\rho C} = 1/T_{1\rho C} + 1/T_{CH}$$

M_e is the ^{13}C equilibrium magnetization obtained when both spin systems fully contact each other without any energy exchange with the lattice and, therefore, this value is proportional to the concentration of a given ^{13}C nucleus in a material. T_{CH} is the time constant for energy exchange between ^1H and ^{13}C spin systems, and $T_{1\rho H}$ and $T_{1\rho C}$ are the spin-lattice relaxation times in their rotating frames. When the ^{13}C magnetization is observed by the CP techniques, T_{CH} should be much shorter than $T_{1\rho H}$ and $T_{1\rho C}$. Under this condition, Eq. (1) reduces to:

$$M_C(t) = M_e[\exp(-t/T_{1\rho H}) - \exp(-t/T_{CH})] \qquad (2)$$

According to this equation, ^{13}C magnetization appears at a rate of the order of $(T_{CH})^{-1}$ and disappears at the rate of $(T_{1\rho C})^{-1}$.

Fig. 3 shows a semilogarithmic plot of the peak intensity as a function of the contact time t for one CH resonance of PVAl and one CH_2 resonance of PCL as representative examples of all the observed resonances with the exception of the carbonyl resonance line of the PCL also shown in the same figure. The intensity maxima are observed at 0.5 and 1 ms, respectively for the PVAl and the PCL. Zhang et al.[13] measured the same contact time at the intensity maximum for PVAl. This value is short compared to the values between 1 and 10 ms generally measured for polymers. This can be explained by the glass behavior of PVAl at room temperature and its auto-association by hydrogen bonds. Cross polarization process, depending on the $^{13}C-H$ dipolar interaction is more efficient for rigid systems since molecular motions reduce the interactions involved. Consequently, T_{CH} will be lower for rigid polymers. This was indeed observed for PVAl and PCL. The carbonyl resonance line of PCL shows the maximum of intensity only after a contact time of 2 ms. This different behavior compared to the other carbons of PCL can be explained by its chemical structure. As this carbon is not bonded to any hydrogen, the cross polarization process occurs from hydrogen atoms located in the near neighborhood. As dipolar interactions are inversely proportional to the interatomic distance C-H, T_{CH} for this carbonyl will increase significantly.

3.9. *CP/MAS* ^{13}C *NMR spectra of PVAl/PCL blends*

Fig. 4 shows CP/MAS ^{13}C NMR spectra measured at room temperature for PVAl, PCL and the 80/20, 50/50, 20/80 PVAl/PCL blends. The spectrum of PVAl shows two groups of resonance which have been attributed to the methine and methylene carbons with increasing magnetic field[12–14]. The methine carbon resonance splits into a triplet with components *a*, *b* and *c* (75, 69.8, 65.1 ppm). The assignment proposed by Terao et al.[14] will be adopted here. The splitting is related to the stereoregularity of the sample and to the intramolecular hydrogen interactions. Resonance *a* has been assigned to triads mm, where the central OH is linked to two first neighbours, resonance *b* to triads mm and mr, where the central OH is linked to one first neighbour and resonance *c* to triads mm, mr and rr, where the central OH is not hydrogen bonded. The spectrum of PCL shows a carbonyl carbon resonance at 173.4 ppm and five methylene carbon resonance (64.3 and 34.0, 28.8, 25.8, 25.0 ppm) numbered from I to V and assigned to the following carbons[15]:

$$\begin{array}{ccccccc} -O- & CH_2- & CH_2- & CH_2- & CH_2- & CH_2- & CO- \\ & \mathrm{I} & \mathrm{III} & \mathrm{V} & \mathrm{IV} & \mathrm{II}. & \end{array}$$

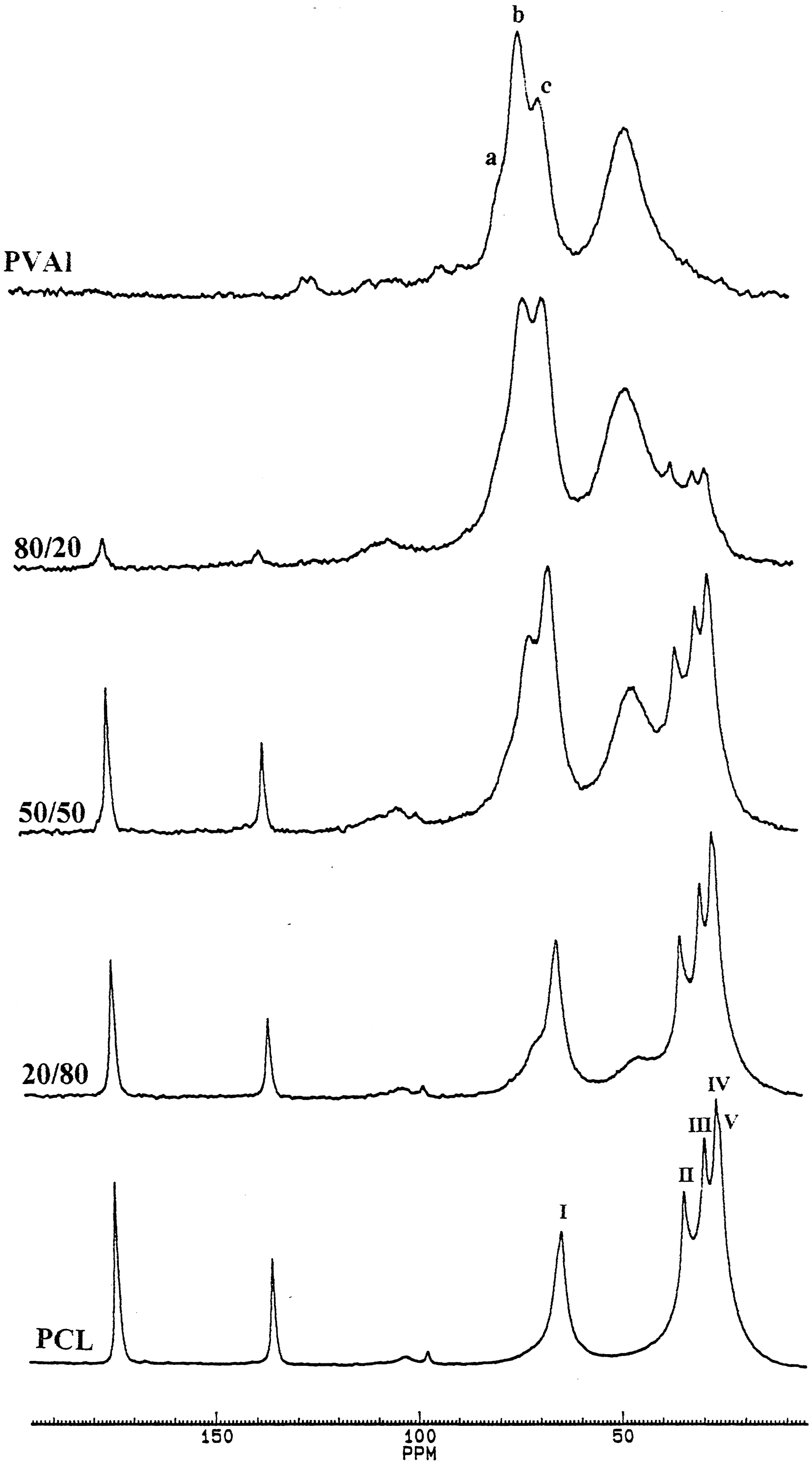


Fig. 4. ^{13}C NMR spectra (DD, CP, MAS) of PCL, PVAl and their blends.

The resonance appearing at 135.7 ppm is a satellite peak of the carbonyl carbon resonance. Interpolymer H-bonding interactions between PVAl and PCL in blends could be identified by changes in the chemical shift of the PCL carbonyl at 173.4 ppm and of the PVAl methine (mainly methine C at 65.1 ppm). In the second case, overlap of the PVAl resonance at 65.1 ppm with the PCL I at 64.3 ppm prevents observation of an eventual displacement of PVAl methine. Such a modification has however been observed by Zhang et al in PVAl-polyacrylic acid[16] and PVAl-polyvinylpyrrolidone blends[13], but we have shown in a preceding paragraph of this paper by DSC and FTIR that the auto-association of PVAl by hydrogen bonds is not disturbed upon blending with PCL. The carbonyl resonance of PCL is well separated from PVAl resonances. However, no significant change of chemical shift is observed as a function of composition. Let us nevertheless remember that the contact time of 0.5 ms used in the CP process does not allow the maximum polarization of these carbons. Furthermore, polarization of the carbonyl carbons located in the rigid crystalline phase of PCL will be favored when compared to the amorphous carbonyl. Consequently, the observed peak will represent more carbonyl groups from the rigid part of PCL. As miscibility is a property of the amorphous phases, we can not excluded hydrogen bond formation between PCL and PVAl by observation on the carbonyl resonance. Measurements of the spin lattice relaxation times of the protons in the blends will allow to determine the importance of interaction between PVAl and PCL.

3.10. Proton spin diffusion and spin lattice relaxation time using cross-polarization

The mean quadratic diffusion distance during a time τ is given by[17]:

$$< r^2 > 6D\tau, \tag{3}$$

where D, the proton spin diffusion coefficient, has a value of 5×10^{-12} cm/s^2[17–19]. Since T_1 and $T_{1\rho}$ have values, respectively, of the order of 1 s and 1 ms, replacing (by these values gives $< r^2 > ^{1/2}$ values of the order of a few tens of nm in the laboratory frame and of a few nm in the rotating frame. If the diffusion length is smaller than the dimension of domains in blends, protons in each component will decay independently of each other and a double exponential decay will be observed. On the contrary, if the diffusion length is much larger than the dimension of the domain in the blend, spin diffusion between both components occur. The observed decay will be monoexponential with a rate K. In the laboratory frame this gives[17]:

$$K = \frac{1}{T_1} = K_{\mathrm{PVAl}}\frac{N_{\mathrm{PVAl}}}{N_{\mathrm{T}}} + K_{\mathrm{PCL}}\frac{N_{\mathrm{PCL}}}{N_{\mathrm{T}}}$$

where N_{i} is the number of protons of polymer i, N_{T} is the total number of protons in the blend and K_{i} ($= 1/T_{1\mathrm{i}}$) is the intrinsic relaxation rate of polymer i.

This equation may be written in terms of the weight, W, of PCL in the blend:

$$(28.4 - W)K = (27.4K_{\mathrm{PCL}} - 28.4K_{\mathrm{PVAl}})W + 28.4K_{\mathrm{PVAl}}. \tag{4}$$

Using this relation, the relaxation time of an intimate blend of PVAl and PCL can be calculated as a function of the composition of the blend.

Table 4 gives the experimental relaxation times T_1 for the pure components and for the blends.They have been measured at 69.8 and 44.2 ppm for PVAl, at 28.8, 25.8 and 25.0 ppm for PCL and at 64.7 ppm for superimposed PVAl and PCL resonance. The theoretical values calculated using Eq. (4) are given in the last column. Examination of the experimental T_1 shows that the pure polymers are characterized by different T_1 (2.9 and 1.1 s for PVAl and PCL, respectively) values which are identical or very near each other on the various carbons. For the blends, the values are intermediate to those of the pure polymers; they are very near each other for the various carbons of each polymer but show some difference on PCL and PVAl carbons. For the 80/20 blend for instance, T_1 is equal to 2.2 s on each PCL carbon, but 2.6 s on each PVAl carbon. The difference between the experimental values and the values calculated using Eq. (4) has now to be considered. A comprehensive view of the results is given in Fig. 5. The 20/80 blend can be considered to be miscible an the scale of T_1; indeed this parameter has very similar values on PCL and on PVAl carbons, these values being similar to the calculated ones. The deviation is larger for the two other blends for which the T_1 values are, nevertheless, intermediate between those of the pure components. We can thus conclude that the scale of compatibility is close to, but somewhat larger than, that of $T_{1\mathrm{blend}}$. Using Eq. (1) values of 60 and 90 nm are obtained for the root mean square average distance $< |r| >$ corresponding to $T_{1\mathrm{PCL}}$ and $T_{1\mathrm{PVAL}}$. The deviation obtained for the PVAl rich blends, can be assigned to a distribution of the domain size in PVAl, some of them being larger than $< |r| >$. PVAl/PCL blends obtained according to the method used in the present work are thus very fine dispersions of one component into the other. Such a very fine dispersion of crystalline glassy PVAl plays an important role by physical interactions on spherulite morphology and degree of crystallization of the later crystallizing PCL as described in the first paragraphs of this paper.

Table 4
Relaxation time of PVAl and PCL protons in the pure polymers and in the blends

Composition PVAl/PCL	$T_{1\mathrm{exp.}}$ (s)						
	δ_{PVAl} (ppm)		$\delta_{\mathrm{PVAl/PCL}}$ (ppm)	δ_{PCL}(ppm)			$T_{1\mathrm{calc.}}$(s)
	69.8	44.2	64.7	28.8	25.8	25.0	
100/0	2.9	2.9	–	–	–	–	–
80/20	2.6	2.6	2.6	2.2	2.2	2.2	2.2
50/50	2.0	2.0	1.9	1.8	1.8	1.8	1.6
20/80	1.3	1.4	1.2	1.2	1.2	1.2	1.3
0/100	–	–	–	1.0	1.1	1.1	–

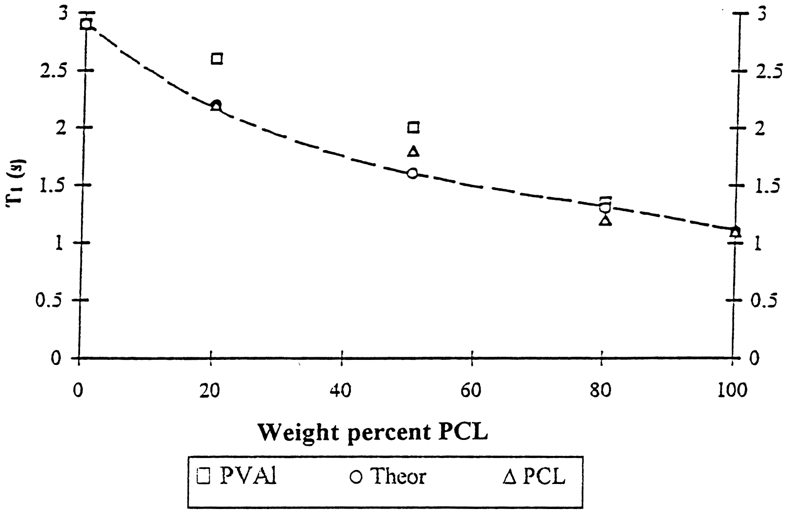


Fig. 5. Proton relaxation time T_1 as a function of blend composition according to data of Table 4.

Acknowledgements

We would like to thank the 'Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et dans l'Agriculture' (IRSIA) and the 'Fondation Universitaire David et Alice Van Buuren' for grants to one of us (C.D.K.). We are also very grateful to Professor F. Lauprêtre, Ecole Supérieure de Physique et de Chimie, Paris and to Professor P. Broekaert, Université Libre de Bruxelles for helpful discussion of the NMR spectra. Mr G. Daelen (FUNDP) is gratefully acknowledged for recording the NMR spectra.

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