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Binary Blends Based on Poly(vinyl chloride) and Multi-Block Copolymers Containing Poly(ε-caprolactone) and Poly(ethylene glycol) Segments

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Summary: Binary blends based on poly(vinyl chloride) (PVC) were prepared both by casting from tetrahydrofuran (THF) and by mixing in the melt form, in a discontinuous mixer, PVC and multi-block copolymers containing poly(ε–caprolactone) (PCDT) and poly(ethylene glycol) (PEG) segments. PCDT-PEG copolymers were synthesized using a polycondensation reaction where the α,ω-bis-chloroformate of an oligomeric poly(ε-caprolactone) diol terminated (PCDT) and oligomeric PEG were employed as macromonomers. For comparison purposes, blends PVC with starting oligomers as well as with mixtures containing a typical low molecular plasticizer, dioctylphthalate (DOP), were also prepared. The copolymer miscibility was studied by differential scanning calorimetry (DSC) and FT-IR spectroscopy. The blend morphology was investigated by polarized light microscopy (PLM). A higher miscibility with PVC was observed for copolymers compared to PEG.

Introduction

The supposed toxicity of most commonly used low molecular weight plasticizers employed to produce flexible PVC has required the development of a new generation of low toxicity flexibilizers. This problem is of great importance in food packaging and in biomedical devices, where the materials are in contact with biological fluids or inserted in the human body.

In this connection, an interesting role might be played by polymeric blends containing a low Tg polymer with a high miscibility with PVC [1, 2]. In principle, the

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high molecular weight of the plasticizer can strongly reduce release processes and toxicity.

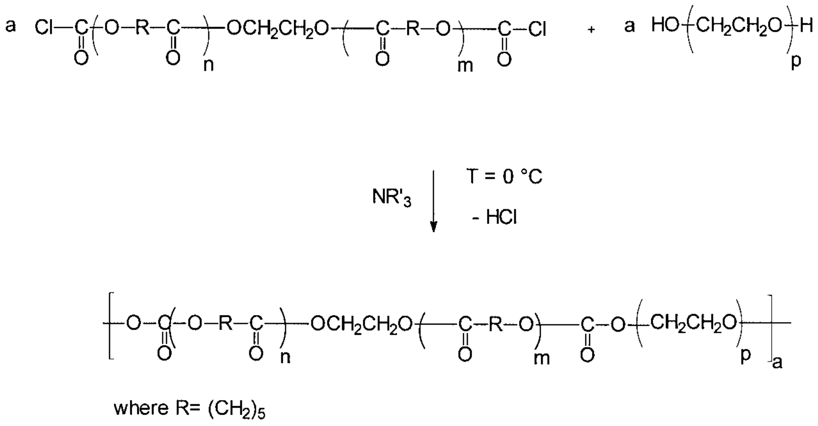
PVC/poly(ε-caprolactone) (PCL) binary blends are interesting systems because some miscibility exists between the components; furthermore PCL is a non-toxic polymer having a low glass transition temperature (Tg). Partial miscibility has been found with high molecular weight PCL and heterogeneous materials with some amount of semi-crystalline PCL phase have been obtained [3, 4].

Biocompatibility is another important factor for materials used in the biomedical field. The PVC biocompatibility has been increased by surface treatments improving its hydrophilicity [5, 6]. To that purpose, given the well-known biocompatibility of PEG, PVC/poly(ethylene glycol) (PEG) blends might be systems of interest, but unfortunately a low miscibility in general exists between these components [7].

The aim of this work is to study the miscibility of PVC with multi-block copolymers containing PCL and PEG segments. Multi-block copolymers were synthesized by a polycondensation reaction between an oligomeric PEG and the α,ω-bis-chloroformate of oligomeric poly(ε-caprolactone) diol terminated (PCDT) (see Scheme). High molecular weight copolymers can be obtained having PCDT and PEG segments linked through carbonate bonds [8-10]. In principle, the miscibility with PVC can be modified changing the length of PCDT and/or PEG blocks. Therefore, two multi-block copolymers having PCDT segments with $\overline{M}_n$ =1250 and PEG with $\overline{M}_n$ = 1000 and 2000 were synthesised.

PVC blends were prepared using two methods. The former involved casting from THF solutions followed by a thermal treatment. The latter was based on melt mixing, in a discontinuous mixer, using a typical industrial recipe employed to produce serum bags. For comparison purposes, blends containing starting oligomers or dioctylphthalate (DOP) were prepared too. Their miscibility and thermal properties were studied by differential scanning calorimetry (DSC) [12, 13] and FT-IR spectroscopy [14, 15].

Scheme



Experimental Part

Instruments

The infrared spectra were recorded by a 5300 Jasco FT-IR spectrophotometer on films obtained by casting from solvent or by compression moulding. ^{1}H NMR spectra were run in deuterared chloroform on a 60 MHz Varian 360 A spectrometer, using TMS as internal reference. Viscometric measurements were performed with a Schott Geräte mod AVS 310 semiautomatic viscometer. The GPC experiments were run on an Erma instrument, using Shodex KF columns, operating with chloroform as eluent, flow rate 1 ml/min and a Knauer RI detector. Calibration curves were obtained by poly(ethylene glycol) standards purchased from Polymer Laboratories, Shropshire (U.K.). The DSC analysis was carried out using a Mettler TC11 Thermal Analyser Processor equipped with a Low Temperature Cell DSC30. The DSC curves were obtained by heating a sample of about 10 mg from - 100 to 100°C at 10°C/min under nitrogen flow (10 ml/min).

Methods

Solubility: Solubility experiments were performed by treating the product (0,05 g) with the solvent (1 ml) for 4 h at room temperature. The mixtures were then warmed up to the boiling point.

Intrinsic viscosity. The intrinsic viscosity was evaluated by using an Ubbelohde viscometer at 32°C in chloroform.

Binary blends by casting: Binary blends were prepared from 5 weight % tetrahydrofyran (THF) (b.p. 66 °C) solutions by solvent evaporation at 25 °C and 760 mmHg for a week. The resulting films were treated first at 90 °C for 8 hours and then at 150 °C for 15 minutes, at 1 mmHg of pressure.

Blends by melt mixing: PVC blends were prepared using a Brabender discontinuous mixer employing a typical industrial recipe used for serum bags production. Mixing conditions: 5 minutes at 160 °C, mixing rate 60 rpm.

Starting materials

PVC having $\overline{M}_n$ *=95000* was purchased from Aldrich Co. (Tg = 85.9 °C).

PEG samples of different molecular weights were purchased from Fluka Co., and dried overnight at 40 °C and 0,1 torr before use.

Poly(ε-caprolactone) diol terminated (PCDT) samples having $\overline{M}_n$ =1250 and 2000 were purchased from Aldrich Co. and dried in vacuum at 0.1 torr for 48 hours.

N-ethyldiisopropylamine (99 wt.-% purity) was purchased from Aldrich Co. and dried over calcium hydride for 48 hours.

4-Dimethylaminopyridine (99 wt.-% purity) was purchased from Aldrich Co. and used as received.

Chloroform was a high-grade commercial product purchased from various sources, not containing ethanol as stabilizer. It was allowed to remain some hours over calcium hydride before use.

All other reagents were high-grade commercial products, used without further purification.

Interlite ZX 9004, Lankroflex E2307, Interwax GP 55, Interwax GP 33, Interwax DP 16 were purchased from Akcros Italia.

Synthesis of PCDT1250-PEG1000 segmented copolymer

13 mL (0.025 mol) 20 wt.-% toluene solution of phosgene was placed, under nitrogen atmosphere, in a flask equipped with a stirrer, a gas inlet which could be lifted at various levels, a gas outlet connected with a sodium hydroxide trap and a dropping funnel with pressure-equalizing side arm, into which a mixture of 12.5 g (0.01 mol) dry PCDT having number-average molecular weight 1250 and 3.52 mL (0.02 mol) N-ethyldiisopropylamine (EDIPA) in chloroform (11 mL) had been charged. The flask was cooled by means of an external bath at 5°C and the solution was added dropwise to the phosgene solution under stirring. After addition, stirring at 5°C was continued for further 15 min, then the gas inlet was lowered and nitrogen bubbled through the reaction mixture for 30 min, in order to eliminate the excess phosgene.

To the resulting solution of PCDT bis(chloroformate), a solution of 10.0 g (0.01 mol) PEG 1000 oligomer, 3.52 mL (0.02 mol) EDIPA and 1.23 g (0.01 mol) 4-dimethyl aminopyridine (DMP) in chloroform (35 mL) were added dropwise under nitrogen atmosphere. The reaction mixture was maintained at 5°C for 8 h under stirring, and then for further 10 h while rising to room temperature. After this time, the solvent was eliminated by evaporating under vacuum. The resulting product was then dissolved in chloroform, precipitated with excess isopropanol and immediately washed with ether. The precipitate was dried at room temperature and 0.1 torr (95 wt.-% yield, $\overline{M}_n$ =33900 and $[\eta] = 0.38$ dL/g).

Synthesis of PCDT1250-PEG2000 segmented copolymer

PCDT1250-PEG2000 segmented copolymer was prepared in the same way as PCDT1250-PEG1000 by substituting PEG having number-average molecular weight 2000 (20 g, 0.01 mol) for PEG 1000. Yield of 95 wt.-% ($\overline{M}_n$ =63500; $[\eta] =$ 0.52 dL/g) .

Characterisations of PCDT1250-PEG1000

IR spectra: the IR spectrum of PCDT1250-PEG1000 showed bands at: 2945-2868 cm^{-1} (ν, CH); 1726 cm^{-1} (ν, C=O); 1300-1000 cm^{-1} (ν, C-C(=O)-O; ν, C-C-O). The IR spectra of PCDT1250-PEG2000, though on the whole qualitatively similar, showed an increase of the relative intensity of the band at 1150-1085 cm^{-1} (ν, C-O-C); the ester band (ν, C=O) is shifted at 1732 cm^{-1}.

^1H-NMR spectra: the ^1H-NMR($CDCl_3$) spectra of PCDT-PEG products showed similar peaks but obviously with different relative intensities. In particular: δ =3.9 – 4.3 (m, CH_2OC=O), δ =3,6 (s; CH_2OCH_2); δ =1.2- 1.9 (m; CH_2-CH_2).

Results and Discussion

1. PCDT/PEG multi-block copolymers

The synthetic process for the preparation of PCDT-PEG segmented copolymers involves the activation of PCDT oligomers by means of phosgene, resulting in the introduction of terminal chloroformate groups. Without isolating, activated PCDTs are then reacted with PEG oligomers, as shown in the scheme. In this way multi-block copolymers having segments linked with carbonate bonds are obtained. We reported this reaction in previous papers dealing with the synthesis of other segmented copolymers based on PLGA. In that case copolymers having a poly(ester-carbonate) structure resulted [8-10].

The molecular weight of oligomeric PEGs employed was selected using a simple miscibility prediction scheme based on the solubility parameters [16, 17]. Values of $[\chi_{AB} - (\chi_{AB})_{cr}]$ *versus* the $\overline{M}_n$ of starting oligomers for blends with PVC ($\overline{M}_n$ = 95000) are shown in Figure 1. Miscibility is expected when this parameter is negative or it equals zero (approximately for $\overline{M}_n \leq 1000$). On the other hand it is well-known that good miscibility can exist in PVC/PCDT blends [18, 19], in agreement with the results of the prediction scheme adopted (Figure 1).

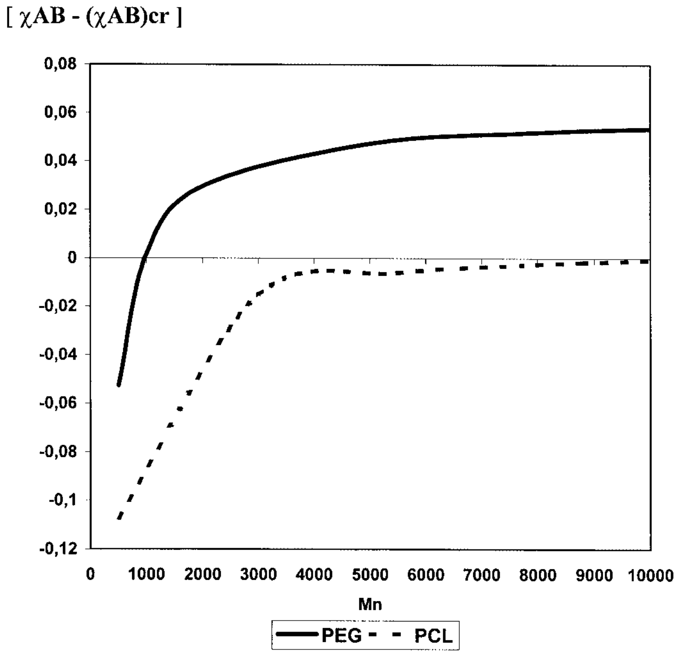


Figure 1: $[\chi_{AB} - (\chi_{AB})_{cr}]$ *versus* $\overline{M}_n$ of starting oligomers for blends with PVC with $\overline{M}_n$ 95000.

Therefore the miscibility of PCDT-PEG copolymers is expected to be considerably influenced by the length of the PEG segments and by the PEG content. On that basis, PEGs with $\overline{M}_n$ 1000 and 2000 were selected. The choice of the $\overline{M}_n$ values for the PCDT oligomers (1250 and 2000) was dictated by their low Tg (-77.7 °C and –60.2 °C, respectively).

The composition, intrinsic viscosity, and thermal properties of the copolymers investigated are reported in Table 1, along with calorimetric data of starting oligomers. It should be noticed that PCDT-PEG copolymers show a single Tg whose value is higher than in starting PCDT.

Table 1: Molecular weight characterisation and DSC data of starting oligomers and block-copolymers

Polymer	**Molecular weight Characterization**				**Calorimetric data**		
	[η] dL/g-	a) $x10^{-3}$	a) $x10^{-3}$	**D**$^{b)}$	**Tg** $^{c)}$ **(°C)**	**Tm** $^{c)}$ **(°C)**	**ΔH** $^{c)}$ **(j/g)**
PCDT 1250	0.09	1.25	-	-	-77.7	58.3	74.9
PEG 1000	-0.03	1.00	-	-	-	38.3	127.0
PEG 2000	-0.09	2.00	-	-	-	56.1	190.0
PCDT1250-PEG1000	0.38	33.90	64.4	1.9	-69.5	45.5	51.8
PCDT1250-PEG2000	0.52	63.50	127.0	2.0	-56.8	40.6	62.4

a) Calculated by SEC using a PEG calibration curve.
b) Polydispersity index: $\overline{M}_w / \overline{M}_n$.
$^{c)}$ under nitrogen (scanning rate: 10°C/min)

Furthermore, a wide fusion peek located in the same temperature range as in PEG and PCDT and having an enthalpy of fusion substantially lower than in starting oligomers was also detected. These data would suggest that some miscibility exists between the PCDT and PEG segments in the above copolymers.

2. PVC blends

Binary blends obtained by casting

Binary blends were prepared by solvent evaporation from THF solutions having a 5 weight % polymer content. The samples were treated first at 90 °C for 8 hours and then at 150 °C for 15 minutes, under vacuum. The composition and thermal properties of the blends prepared are summarized in Table 2. The percentage of crystallinity of PEG in the blends in comparison with that of pure oligomer was evaluated according to the equation: $C = \Delta H_m \cdot 100/w \cdot \Delta H^\circ_m$; where ΔH°_m is the heat of fusion of starting oligomers or copolymers, w is their weight fraction in the blend and ΔH_m is the heat of fusion of the blend.

Table 2: DSC data of PVC blends obtained by casting

Polymer		**Calorimetric data**[a)]				
Type	**wt-%**	**Tg** (°C)	**Tm** (°C)	**ΔH** (j/g)	**C**[b)] (%)	**ΔTm**[c)] (°C)
PVC	-	81.0	-	-	-	-
PEG 1000	10	48.7	28.7	1.4	11	9.6
PEG 1000	20	44.5	35.0	1.9	8	3.3
PEG 1000	30	44.0	33.6	19.3	51	4.7
PEG 2000	10	42.5	47.5	1.6	8	8.6
PEG 2000	20	-	49.3	15.2	40	6.8
PEG 2000	30	-	50.9	28.4	50	5.1
PCDT 1250	10	39.0	-	-	-	-
PCDT 1250	20	-8.5	-	-	-	-
PCDT 1250	30	-23.5	-	-	-	-
PCDT-PEG1000	20	11.0	-	-	-	-
PCDT-PEG2000	20	-33.0	42.6	2.0	16	-2.0

a) under nitrogen (scanning rate: 10°C/min)

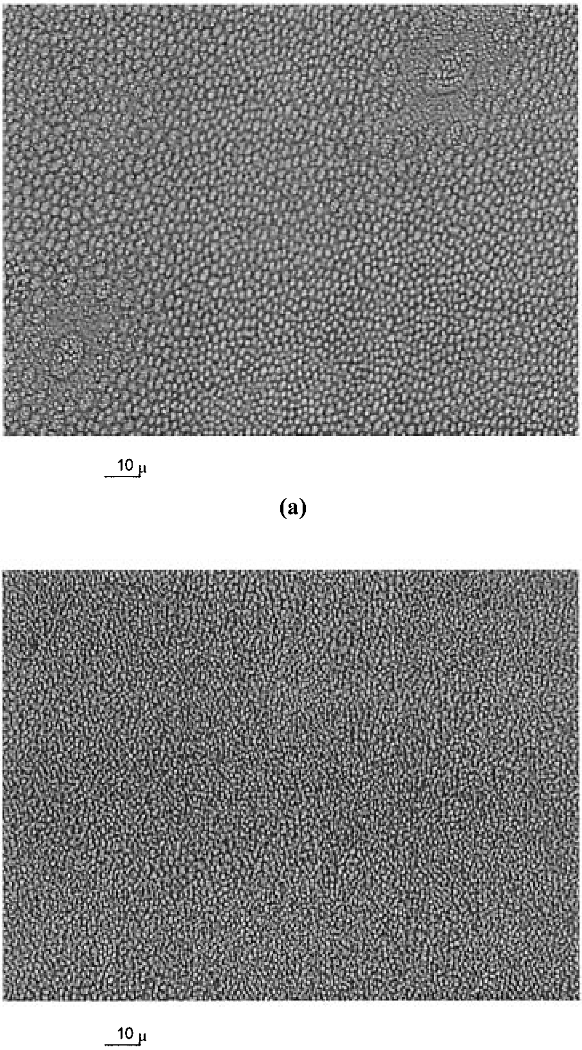
b) Percentage of crystallinity evaluated by means of the following equation: $C = \Delta H_m \cdot 100/w \cdot \Delta H^\circ_m$ where ΔH°_m is the heat of fusion of starting oligomers or copolymers, ΔH_m is the heat of fusion of the blend and w is the their weight fraction in the blend.

c) melting temperature depression: Tm° - Tm , where Tm° and Tm are the melting point of pure crystallisable component and of blend respectively.

The calorimetric data of PVC/PEG blends show a very limited miscibility. Even if all materials contain a crystalline PEG phase, these data suggest that PEG1000 is more miscible with PVC than PEG2000. In fact, crystallinity values of 11%, 8%, 51 %, and 8%, 40%, 50% were calculated for blends containing 10, 20 and 30 weight-% of PEG1000 and PEG2000, respectively. On the contrary, only a limited difference exists between the melting depression temperature (ΔTm) of these two series. For instance ΔTm is 9.6°C and 8.6°C for PVC/PEG1000 and PVC/PEG2000 with a 10 weight-% oligomer content, respectively. An anomalous value of ΔTm is exhibited by PVC/PEG1000 (20 weight-%) as a ΔTm near to that of PVC/PEG2000 is expected. Tg's in the range of 40 ÷ 50°C were in general detected. FT-IR spectroscopy confirms the existence of some degree of interaction between PVC and PEG1000; in fact, the ether band is shifted from 1109 cm^{-1} (pure PEG 1000) to 1103 cm^{-1} (20 weight-% PVC/PEG1000).

On the other hand, full miscibility exists in PVC/PCDT1250 blends within the range of compositions examined. All blends are amorphous materials showing a single Tg, the value of which decreases with the PCDT content from 40°C to 25°C. FT-IR spectroscopy shows a shift of the ester band from 1724 cm^{-1} (pure PCDT1250) to 1732 cm^{-1} (10 weight-% PVC/PCDT1250). This shifting is ascribed to hydrogen bond interactions occurring between PVC and PCDT.

The miscibility of PCDT-PEG copolymers with PVC is strongly dependent on the length of the PEG segments, *i.e.* on their weight fraction. In fact, the PVC/PCDT-PEG1000 blend does not show appreciable crystallinity and displays a single Tg at 11 °C, a value substantially lower than in the PVC/PCDT1250 blend containing the same amount of PCDT (10 weight-% of PCDT1250, Tg = 39 °C). In contrast, a peek of fusion appears in PVC/PCDT-PEG2000. The lower melting point (Tm = 42.6 °C) compared to the PVC/PEG2000 blend having a comparable PEG2000 content (10 weight-%, Tm = 47.5 °C) suggests that some miscibility exists. The morphological analysis, performed by polarized light microscopy, confirms that the PEG2000 miscibility is increased if a multi-block copolymer is employed (see Figure 2.a and 2.b). The FT-IR analysis shows a shift of the ester and ether bands, as observed in PVC/PCDT and PVC/PEG blends.



(a)

(b)

Figure 2: Polarized light microscopy (PLM) of PVC/PEG2000 10 wt.-% (a) and PVC/PCDT-PEG2000 20 wt.-% blends.

Blends by mixing melt

PVC blends were prepared using a Brabender discontinuous mixer at 160 °C employing a typical industrial recipe used for serum bags production (see Table 3).

Table 3: Typical recipe used in the discontinuous mixer

Product	weight (g)	
PVC	34.00	28.00
Plasticizer	6.00	12.00
INTERLITE ZX 9004a) (Ca/Zn stabilizer)	0.68	0.56
LANKROFLEX E2307a) ‘Epoxidized soya bean oil)	1.36	1.12
INTERWAX GP 55a) (Lubricant)	0.68	0.56
INTERWAX GP 33Va) (Lubricant)	0.34	0.28
INTERWAX GP 16a) (Lubricant)	0.34	0.28

a) Products purchased from AKCROS CHEMICALS

In particular, mixtures containing oligomeric PCDT 2000 and DOP were prepared for comparison with PVC/PCDT-PEG. The thermal properties of blends, evaluated by means of DSC, are summarized in Table 4. A high miscibility is noticed in systems containing oligomeric PCDT. In fact, the blends exhibit optical clarity and only a single Tg whose value strongly depends on the composition. For instance, a Tg of 6.6°C and -22.2°C is observed for the 15 and 30 weight-% content of oligomer, respectively. It should be noticed that the latter Tg is very close to that of the PVC/DOP blend with the same amount of plasticizer (Tg = -20.8). No melting peeks are observed in these materials.

Only a single Tg is detected in blends containing PCDT-PEG1000 (*i.e.* –11 °C in the sample at 30 %). Also, no appreciable crystallinity is present and optical clarity is observed. Therefore, it is possible to say that a high miscibility is maintained even when typical additives are added.

In the blend containing PCDT-PEG2000 a lower miscibility is observed. In fact, the DSC traces show the presence of a crystalline phase probably related to the PEG blocks (Tm = 38.1°C).

Table 4: PVC blends obtained in Brabender mixer

Plasticizer		**Calorimetric data** [a]		
Type	**Wt.-%**	**Tg (°C)**	**Tm (°C)**	**ΔH (j/g)**
DOP	15	-9.1	-	-
DOP	30	-20.8	-	-
PCDT 2000	15	6.6	-	-
PCDT 2000	30	-22.2	-	-
PCDT1250-PEG1000	30	-11.6	-	-
PCDT1250-PEG2000	30	-30.9	38.1	1.7

[a] under nitrogen (scanning rate: 10°C/min)

Conclusions

Binary blends based on PVC were prepared by casting using multi-block copolymers containing PCDT and PEG segments. The synthetic scheme employed gives the opportunity of tailoring the miscibility between the copolymers and PVC. In fact, the presence of the PCDT blocks increases the miscibility of the PEG segments. A process of melt mixing, employing typical calcium/zinc stabilizers, leads to results in agreement with those obtained by casting.

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