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DSC studies of poly(vinyl chloride)/poly(ε-caprolactone)/poly(ε-caprolactone)-b-poly(dimethylsiloxane) blends

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Abstract Poly(vinyl chloride)/poly(ε-caprolactone)/poly(ε-caprolactone)-b-poly(dimethylsiloxane) [PVC/PCL/(PCL-b-PDMS)] blends were prepared by solvent casting from tetrahydrofuran. The content of PVC was kept constant (60 wt%); the PCL and PCL-b-PDMS contents were varied by replacing different amounts of PCL [0–20 wt% from the PVC/PCL (60/40) blend] with PCL-b-PDMS copolymer having different molecular weights of the PCL blocks. The thermal properties of prepared blends were investigated by differential scanning calorimetry in order to analyse miscibility (through glass transition temperature) and crystallinity. Differential scanning calorimetry analyses show that the PVC/PCL/PCL-b-PDMS blends are multi-phase materials which contain a PVC plasticized with PCL phase, a block copolymer PCL-b-PDMS phase (with crystalline and amorphous PCL and PDMS domains) and a PCL phase (preponderantly crystalline).

Keywords Poly(vinyl chloride) · Poly(ε-caprolactone) ·
PCL-b-PDMS diblock copolymers · Polymer blend · DSC · Crystallization

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Introduction

Poly(vinyl chloride) (PVC) is a linear, thermoplastic, substantially amorphous polymer, with a huge commercial interest, due to the accessibility to basic raw materials and to its properties [1]. When plasticized, PVC presents some interesting properties which make it widely accepted for use in flexible medical products (dialysis, blood, urine and secretion bags, blood tubing for hemodialysis, endotracheal tubes, intravenous solution dispersion set, catheters, contact lenses, gloves, as well as for drug product storage and packaging) [2]. In addition, many other PVC medical devices have passed critical toxicological, biological and physiological tests [3].

From the large number of plasticizers for PVC, the class of phthalic acid esters, mainly di(2-ethylhexyl) phthalate (DEHP), is widely used for medical devices as a result of their cost convenience and adaptability [4]. Nevertheless, since these plasticizers are low-molecular substances and not covalently bonded to the polymer, they can leach from the matrix, inducing toxicity problems and a loss of plasticizing effect. Another risk concerns the interactions between DEHP and some substances that are contained in the fluids coming in contact with the plasticized PVC [5].

An efficient way to solve the problem of human exposure to DEHP from plasticized PVC is the use of polymeric plasticizers instead of low molecular ones. This method is based on the fact that polymeric plasticizers present low volatility, high resistance to extraction and low migration at high temperatures [6].

Among the polymeric plasticizers that can be used for PVC, the aliphatic polyesters are of great interest, especially poly(ε-caprolactone) (PCL). The PVC/PCL blends are tougher, more extensible than those prepared with conventional plasticizers, with better drape, softness and higher resistance to extraction by oil and water [7].

To confer hemocompatibility, polysiloxanes can be added to these blends, especially poly(dimethylsiloxane) (PDMS), which are extremely interesting materials since they possess many attractive properties, such as extremely low glass transition temperatures (around -120 °C), very high chain flexibility, good oxidative, thermal and UV stability, hydrophobicity, biocompatibility, high gas permeability, low surface energy, high lubricity and excellent atomic oxygen plasma resistance [8].

Due to their very large volumes, low cohesive energy densities and high chain flexibility, PDMS show extremely low surface energies and very low solubility parameters, being immiscible with most organic polymers. As a result of their incompatibility and surface activity, when the siloxanes are blended with various organic polymers, the air-polymer surfaces of the resulting systems are dominated by the low surface energy siloxane [9]. Even at very small levels of bulk siloxane content (0.5–5.0 wt%), the resulting blends display completely silicon-like surface properties.

In practice, PDMS has little use for surface modification by blending, due to its incompatibility with almost all organic based polymers, which leads to their exudation from the system over a period of time. Therefore, siloxane homopolymers can at best provide a temporary surface modification to the blend. An effective way to increase the compatibility of such blends is to form block copolymers of siloxanes with other polymers [10]. Due to their multiphase morphology, these copolymers bring the interesting properties of siloxanes in addition to the desirable mechanical properties of the organic polymers they are combined with [11]. In such systems, the organic component of the siloxane copolymers provides miscibility with the based polymer, while the siloxane segments migrate to the air-polymer surface. Therefore, these organic segments act as "anchoring groups" for siloxane blocks providing a permanent surface modification [10, 11].

Among the copolymers based on PDMS and PCL, the PCL-b-PDMS diblock copolymers are of great interest, because they combine the surface modifying characteristic of PDMS with the compatibilizing effect of PCL. However, PCL is a semi-crystalline polymer, so that, a part of the PCL component of the blend is able to separate into a crystalline phase.

In this work, we have blended PCL-b-PDMS diblock copolymers with PVC and PCL homopolymers and investigated their miscibility and crystallinity by differential scanning calorimetry (DSC).

Experimental part

Materials

Poly(vinyl chloride) (PVC, Mw = 78,000 g/mol, Oltchim S.A., Râmnicu Vâlcea, Romania), poly(ε-caprolactone) (PCL, Fluka, Mw = 10,000 g/mol) and tetrahydrofuran (THF, 99%, Acros Organics) were used as received. The linear diblock copolymers poly(ε-caprolactone)-b-poly(dimethylsiloxane) (PCL-b-PDMS) were prepared in our laboratory, their characteristics being presented in Table 1 [12].

Polymer blends preparation

The polymer blends were prepared by solvent casting from THF solutions with a total polymer concentration of 5 wt%. Given volumes of each component,

Table 1 Characteristics of the different PDMS-b-PCL diblock copolymers

Sample	$\overline{M}^{a}_{nPCL}$	$\overline{M}^{a}_{nPDMS}$	$\overline{M}_n$ copolymers^a	$\overline{M}_n$ copolymers^b	PDI^b	PCL content, wt%	PDMS content, wt%
D_1	500	4,900	5,400	5,700	1.08	10.2	89.8
D_2	700	4,900	5,600	6,200	1.22	12.5	87.5
D_3	2,100	4,900	6,700	8,400	1.10	31.4	68.6
D_4	3,100	4,900	8,000	13,000	1.16	38.8	61.2
D_5	5,100	4,900	10,100	10,100	1.17	51.5	48.5
D_6	7,300	4,900	12,200	16,400	1.12	59.8	40.2
D_7	10,500	4,900	15,400	15,600	1.14	68.2	31.8

[a] Determined by ^{1}H NMR

[b] Polydispersity indices determined by SEC using a PS calibration curve

Table 2 Compositions of PVC/PCL/(PCL-b-PDMS) blends (wt%), the content of PVC being kept constant (60 wt%)

	PCL (%)	PCL-b-PDMS (%)
D_0-0	40	–
D_i-1	36	4
D_i-2	32	8
D_i-3	28	12
D_i-4	24	16
D_i-5	20	20

D_i diblock copolymers code according to Table 1

calculated to obtain film of 0.3 mm thickness, were mixed together for 30 min, under magnetic stirring. The solutions were poured into Teflon moulds 60 mm in diameter, and THF was slowly evaporated under ambient conditions. The resulting films were dried in a vacuum oven for 72 h at 40 °C.

There were prepared binary PVC/PCL and ternary PVC/PCL/(PCL-b-PDMS) blends. In binary blends, the PCL content was 40 wt%. In ternary blends, the content of PVC was maintained constant (60 wt%) and varied the PCL and PCL-b-PDMS contents: one part of PCL (4, 8, 12, 16 and 20 wt%) was replaced with PCL-b-PDMS, as shown in Table 2.

In Table 3 are given the real percentages of the different polymers (PVC, PCL, PDMS) of the blends.

Characterization

Thermal properties of blends were investigated by differential scanning calorimetry (DSC), on a Mettler Toledo DSC 822^e equipment, and thermograms were recorded between -140 and $+140$ °C at a heating rate of 10 °C/min. The DSC samples were first heated under nitrogen atmosphere to $+140$ °C, and then quenched to -140 °C using liquid nitrogen. The heating/cooling cycle was repeated two times. The reported thermograms were taken from the second heating run.

Results and discussion

The DSC thermograms of pure PVC and PCL, of PCL-b-PDMS diblocks (sample D_4, see Table 1 for composition), and PVC/PCL blend (60/40) and PVC/PCL/PDMS-b-PCL blend (60/28/12) (D_2-3, see Table 3 for composition) are shown in Fig. 1. The arrows in the figure show the position of the glass transition temperatures (T_g) and of the endothermic melting peaks of the different blend components.

The DSC for pure PVC reveals only the glass transition temperature (T_g) of 86.7 °C, while that of pure PCL, the T_g of -61.9 °C and an endothermic peak at 56.4 °C corresponding to the melting temperature (T_m).

The DSC thermogram of the PVC/PCL blend shows a single T_g at 1.8 °C and a endothermic peak with a T_m of 60.8 °C. The presence of only one T_g, lower than the T_g of PVC, and higher than the T_g of PCL clearly indicates that PCL (which is

Table 3 Real percentages (wt%) of the different blends constituents, the PVC content being kept constant (60 wt%)

Sample	PCL (%)	PDMS (%)
D_0-0	40	–
D_1-1	36.4	3.6
D_1-2	32.7	7.3
D_1-3	29.1	10.9
D_1-4	25.5	14.5
D_1-5	21.9	18.1
D_2-1	36.7	3.3
D_2-2	33.4	6.6
D_2-3	30.0	10
D_2-4	26.7	13.3
D_2-5	23.4	16.6
D_3-1	37.1	2.9
D_3-2	34.3	5.7
D_3-3	31.5	8.5
D_3-4	28.6	11.4
D_3-5	25.8	14.2
D_4-1	37.5	2.5
D_4-2	35.0	5.0
D_4-3	32.6	7.4
D_4-4	30.1	9.9
D_4-5	27.6	12.4
D_5-1	38.0	2.0
D_5-2	36.0	4.0
D_5-3	34.0	6.0
D_5-4	32.0	8.0
D_5-5	30.0	10.0
D_6-1	38.4	1.6
D_6-2	36.7	3.3
D_6-3	35.1	4.9
D_6-4	33.4	6.6
D_6-5	31.8	8.2
D_7-1	38.8	1.2
D_7-2	37.4	2.6
D_7-3	36.1	3.9
D_7-4	34.8	5.2
D_7-5	33.4	6.6

compatible with PVC) acts as plasticizer for PVC. The T_g observed at 1.8 °C is higher than the value mentioned in literature (−31.1 °C) for a (60/40) PVC/(DEHP) composition [13].

The melting temperature very close to T_m of pure PCL indicates that only a part of PCL acts as plasticizer for PVC [7]. The difference of 4.4 °C between the T_m of

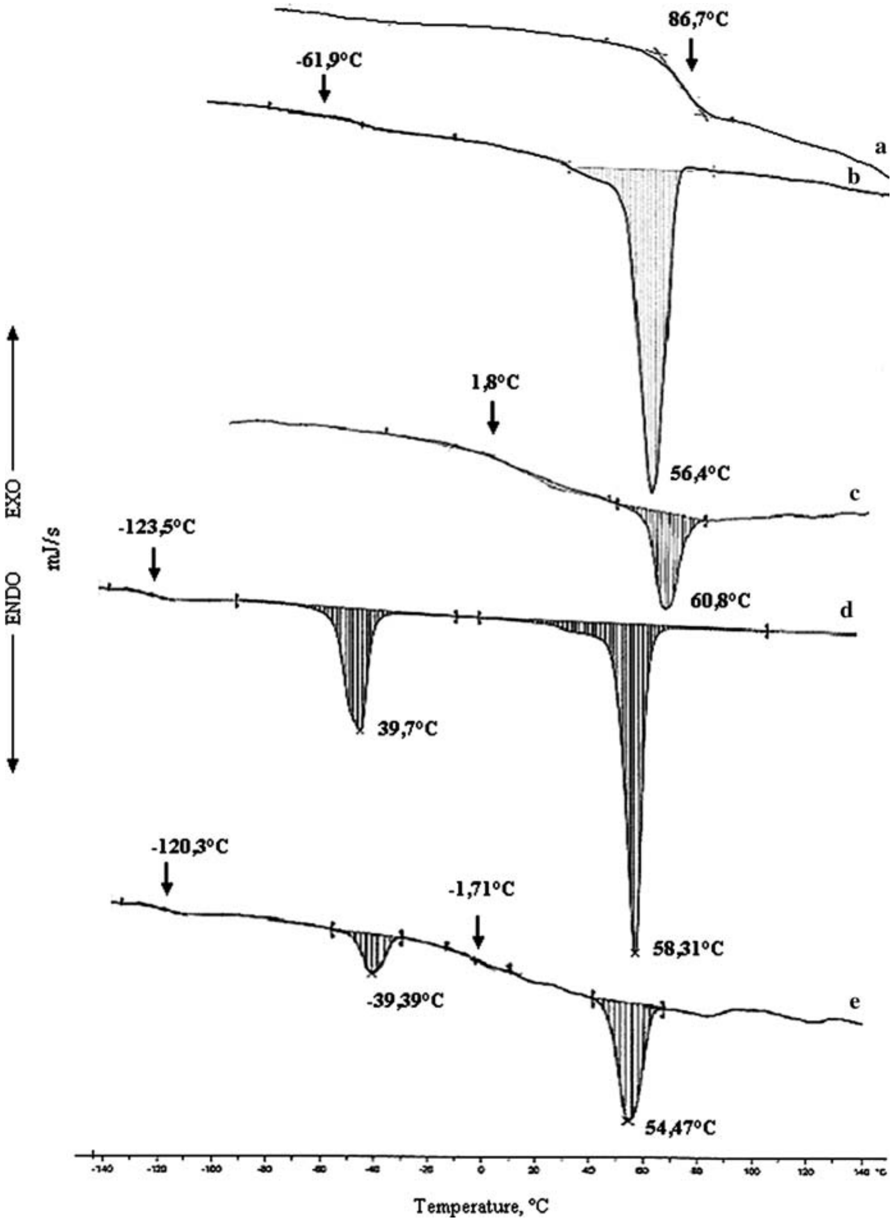

Fig. 1 DSC thermograms of PVC (**a**), PCL (**b**), PVC/PCL blend (60/40) (**c**), PCL-b-PDMS D_4 (**d**) and PVC/PCL/PDMS-b-PCL blend (60/28/12) D_2-3 (**e**)

the crystalline structures of PCL from the PVC/PCL blend and that of pure PCL can be explained by the fact that the crystalline structure of PCL is modified when blended with PVC. This means that the PCL/PVC blend is a biphasic system (with a two-phase morphology) in which coexist a homogeneous amorphous phase, of PVC plasticized with PCL, and a crystalline one of PCL. Similar results were obtained in other studies [13–16].

The DSC thermogram for the PCL-b-PDMS diblocks shows a T_g at −123.5 °C attributed to the PDMS block (for the PDMS homopolymer, the T_g is equal to −124.4 °C [10]) and two endothermic peaks at −48.7 and 54.5 °C. The first peak can be attributed to the melting of the PDMS crystalline structure, while the second one corresponds to the melting of the PCL crystalline structure.

The thermal characteristics evidenced by this thermogram permit the conclusion that PCL-b-PDMS is a phase segmented material in which an amorphous domain and crystalline structures, corresponding to PCL crystals and PDMS crystals, exist. This morphology mainly results from incompatibility of the two blocks in the copolymer. Other researchers [17] who synthesized this kind of block copolymers have reached the same conclusion.

The DSC thermogram for the PVC/PCL/PCL-b-PDMS blend shows two T_g values and two melting peaks. The T_g at −120.3 °C corresponds to PDMS while that at −1.71 °C corresponds to the plasticized PVC with PCL. This T_g, lower than the one obtained for the PVC/PCL blend (1.8 °C) results from the participation of the PCL present in the block copolymer as a plasticizer for PVC. The endothermic peak present at −39.3 °C corresponds to the melting of the PDMS block, and the one at 54.5 °C corresponds to PCL melting.

The thermal characteristics obtained from DSC analyses show that the PVC/PCL/PCL-b-PDMS blend is a multi-phase material [18–20] which contains a PVC plasticized (with PCL) phase, a block copolymer PCL-b-PDMS phase (with crystalline and amorphous domains) and a PCL phase (preponderantly crystalline). Each of these phases has its own influence on the material characteristics.

DSC analyses were performed for all blends (whose compositions are presented in Table 3), to show the influence of both the amount of block copolymer and the length of the PCL block of the diblocks on the blends properties. The thermograms, recorded over the interval −120 °C +120 °C, show only one glass transition temperature (corresponding to the PVC plasticized with PCL) and the melting of both PDMS and PCL. All these thermograms (presented on Fig. 2 for some blends, as examples) evidence the thermal characteristics (T_g, melting peaks) discussed above for sample D_2-3.

The theoretical glass temperatures (T_{gt}) were predicted according to the Fox Equation (Eq. 1 [21]) without taking into account the presence of PDMS (incompatible with PVC), and without taking into account, in a first approximation, the crystallization of PCL:

$$1/T_{gt} = \omega_1/T_{g1} + \omega_2/T_{g2} \tag{1}$$

where ω_1 and ω_2 are the weight fractions of the PVC and PCL blend components, and T_{g1} and T_{g2} represent the glass temperatures of PVC and PCL, respectively.

The experimental T_g (measured by DSC) and the theoretical T_g are given in Table 4 for the different blends.

Analysis of the results presented in Table 4 shows that T_{gt} increases with increasing the block copolymer amount (from D_i-1, 4% to D_i-5, 20%), due to decrease of the total PCL amount from the blends (homopolymer and PCL block).

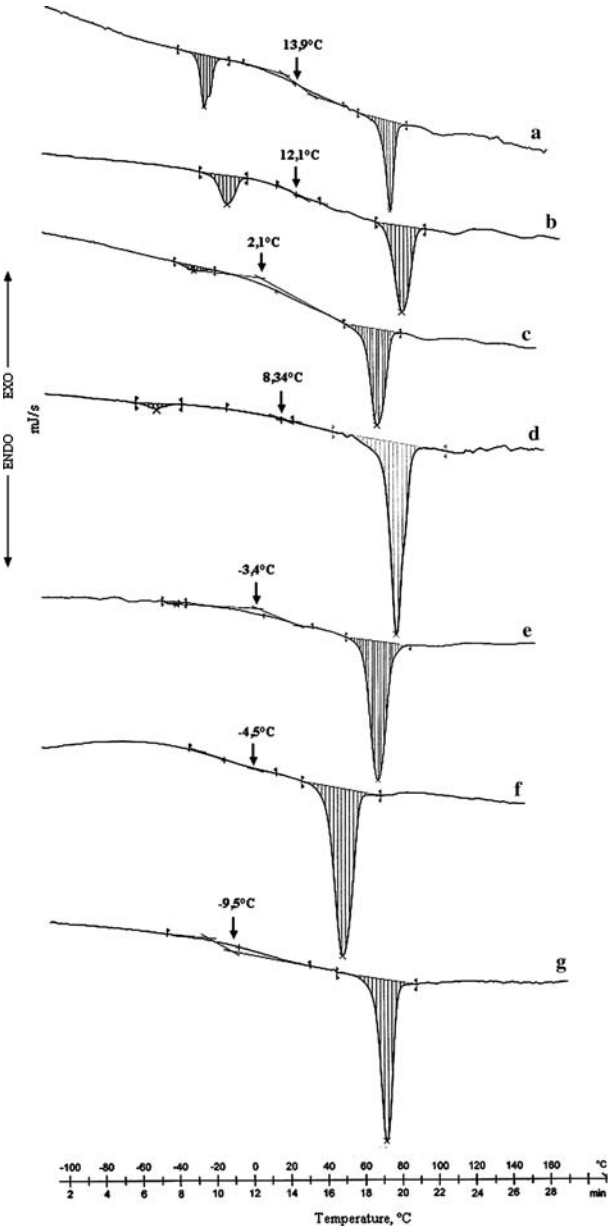

Fig. 2 DSC thermograms for PVC/PCL/PCL-b-PDMS blends with the same amount of block copolymer but with different molecular weights of the PCL block: D_1-3 (**a**), D_2-3 (**b**), D_3-3 (**c**), D_4-3 (**d**), D_5-3 (**e**), D_6-3 (**f**), D_7-3 (**g**)

The same results indicate that T_{gt} decreases with increasing the molecular weight of the PCL block (from D_1-i, $M_{nPCL} = 500$ g/mol to D_7-i, $M_{nPCL} = 10{,}500$ g/mol) (Fig. 3).

Table 4 T_g of PVC/PCL/(PCL-b-PDMS) blends : experimental (DSC) and theoretical values

	PCL (%)	T_g (°C) ± 1	
		DSC	Theoretical
D_0-0	40	2	8
D_1-1	36.4	8	11
D_1-2	32.7	9	15
D_1-3	29.1	14	19
D_1-4	25.5	19	24
D_1-5	21.9	24	30
D_2-1	36.9	5	11
D_2-2	33.4	8	14
D_2-3	30.0	12	18
D_2-4	26.7	22	23
D_2-5	23.4	21	27
D_3-1	37.2	3	10
D_3-2	34.3	5	13
D_3-3	31.5	2	17
D_3-4	28.6	6	20
D_3-5	25.8	9	24
D_4-1	37.5	0	10
D_4-2	35.0	0	13
D_4-3	32.6	8	15
D_4-4	30.8	7	17
D_4-5	27.6	5	21
D_5-1	38.0	−10	10
D_5-2	36.0	−5	12
D_5-3	34.0	−3	14
D_5-4	32.0	−1	16
D_5-5	30.0	3	18
D_6-1	38.4	−10	9
D_6-2	36.7	−5	11
D_6-3	35.1	−5	13
D_6-4	33.4	−6	14
D_6-5	31.8	4	16
D_7-1	38.8	−6	9
D_7-2	37.4	−4	10
D_7-3	36.1	−1	12
D_7-4	34.8	−2	13
D_7-5	33.4	2	14

The experimental glass temperature values (T_{gDSC}) are lower than those calculated theoretically. The difference, varying between 3 and 12 °C, generally increases with increasing the molecular weight of the PCL block, indicating that the

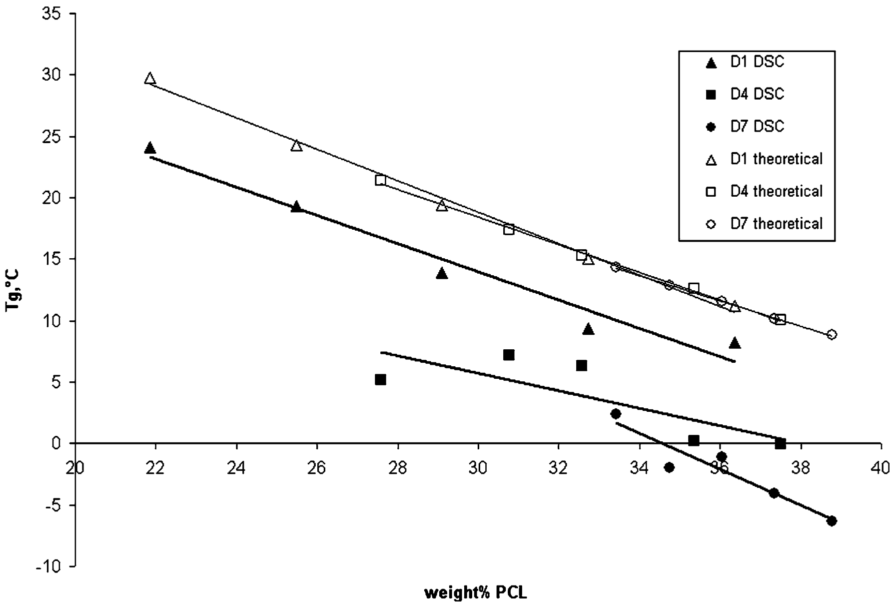

Fig. 3 T_g as a function of PCL content in PVC/PCL/PCL-b-PDMS blends

presence of a PDMS block influences the interactions between PCL and PVC, thus contributing to the plasticizing process.

The T_{gDSC} values are quite dispersed, but they show the same tendency of decreasing with increasing the molecular weight of PCL block and increasing with the PCL content in the blends.

Differential scanning calorimetry data on the melting temperature (T_m) and crystallinity degree (X_{cr}) for PCL and PDMS are shown in Table 5.

It was observed that the endothermic peak corresponding to the PDMS block no longer appears on the DSC thermograms for the blends in which the molecular weight of the PCL from the diblock copolymers exceeds 3,100 g/mol (from $D_{5\text{-}i}$ to $D_{7\text{-}i}$ samples). We considered that, in these cases, the crystalline structures of PDMS blocks are destroyed, along with their blending with PVC and PCL.

The T_m values of the PDMS blocks (in which the endothermic peak is visible) are close to the T_m of pure PDMS (41.3 °C). This means that crystalline structure of the PDMS is not modified when block copolymers are incorporated into the blends.

The endothermic peak corresponding to PCL appears on all DSC thermograms, with T_m's close to the T_m of the homopolymer (56.4 °C). This means that the crystalline structure of the PCL is not dramatically modified when block copolymers are incorporated into the blends.

The crystallinity degrees (X_{cr}) of PCL and PDMS were calculated by dividing the melting enthalpy corresponding to each polymer [corresponding to the real amount of each component from the blend (Table 3)] by the reference enthalpy of a totally crystalline polymer (142 J/g for PCL [22] and 63.4 J/g for PDMS [23]). The X_{cr} values for PCL and PDMS are presented in Table 5.

Table 5 Melting temperature (T_m) and crystallinity degree (X_{cr}) for PCL and PDMS

	PCL %	Melting temperature (T_m, °C, ± 1)		Crystallinity degree (X_{cr}, %, ±3)	
		PDMS	PCL	PDMS	PCL
D_0-0	40	–	61	–	9
D_1-1	36.4	−42	56	48	16
D_1-2	32.7	−42	56	56	16
D_1-3	29.1	−43	56	56	13
D_1-4	25.5	−43	57	57	11
D_1-5	21.9	−42	53	55	8
D_2-1	36.7	−44	56	50	25
D_2-2	33.4	−44	56	45	22
D_2-3	30.0	−44	55	47	20
D_2-4	26.7	−45	54	45	16
D_2-5	23.4	−45	50	47	13
D_3-1	37.2	−46	56	25	20
D_3-2	34.3	−46	56	29	22
D_3-3	31.5	−43	55	14	24
D_3-4	28.6	−42	54	26	16
D_3-5	25.8	−44	–	36	–
D_4-1	37.5	−42	57	52	18
D_4-2	35.0	−42	56	42	29
D_4-3	32.6	−45	55	52	–
D_4-4	30.8	−46	55	36	29
D_4-5	27.6	−46	54	39	31
D_5-1	38.0	–	54	–	35
D_5-2	36.0	–	56	–	31
D_5-3	34.0	–	56	–	31
D_5-4	32.0	–	55	–	23
D_5-5	30.0	–	56	–	15
D_6-1	38.4	–	56	–	52
D_6-2	36.7	–	56	–	56
D_6-3	35.1	–	55	–	42
D_6-4	33.4	–	-	–	–
D_6-5	31.8	–	58	–	20
D_7-1	38.8	–	55	–	22
D_7-2	37.4	–	55	–	20
D_7-3	36.1	–	57	–	28
D_7-4	34.8	–	54	–	36
D_7-5	33.4	–	58	–	50

The results show that the X_{cr} of PDMS and PCL depends on the amount of block copolymer and the length of the PCL block of the diblocks in the blends. A high degree of dispersion of PDMS and PCL crystallinity degrees is observed for the analyzed blends. However, general tendencies can be establish from these results.

When increasing the molecular weight of the PCL block (from D_1 to D_5), the X_{cr} of PDMS globally decreases (see Table 5). Further DSC measurements have been performed with slower cooling rates. In all cases, PDMS and PCL crystallinities were not affected by the cooling rate.

It may be stated that the X_{cr} of PCL generally increases with increasing the molecular weight of the PCL block from the block copolymers (Table 5). This increase of X_{cr} with PCL block length is more pronounced for D_5 and D_6. For the blends obtained with these copolymers, the absence of PDMS blocks organization can favour the organization of PCL blocks, explaining their higher crystallinity degree. Concerning the effect of the amount of block copolymers, a higher content of diblock generally induces a decrease of PCL crystallinity (excepted for D7).

For blends containing D_7, a more complex behavior is observed. Copolymer D_7 corresponds to a PCL length equal to 10,500 g/mol, which is the length of the PCL homopolymer of the blend. In that case, more complicated crystallization processes (co-crystallization of PCL block with PCL homopolymer) probably occur. Further studies are then needed to better understand thermal properties of D_7 blends.

Conclusions

PVC/PCL/(PCL-b-PDMS) blends were prepared by solvent casting from THF solutions. The content of PVC was kept constant (60 wt%), and the PCL and PCL-b-PDMS contents were varied by replacing different amounts of PCL [0–20 wt% from the PVC/PCL (60/40) blend] with PCL-b-PDMS copolymer having different molecular weights of the PCL blocks.

The thermal properties of prepared blends were investigated by differential scanning calorimetry in order to analyse miscibility (through glass transition temperature) and crystallinity.

Differential scanning calorimetry analyses show that the PVC/PCL/PCL-b-PDMS blends are multi-phase materials which contain a PVC plasticized with PCL phase, a block copolymer PCL-b-PDMS phase (with crystalline and amorphous PCL and PDMS domains) and a PCL phase (preponderently crystalline).

The T_{gDSC} values show the same tendency of decreasing with increasing the molecular weight of PCL block and increasing with the PCL content from the blends, indicating that the PCL from diblock copolymers contributes to the plasticizing process. Crystallinity of PDMS block disappears when the PCL and PDMS blocks length become similar. In the future, it would be interesting to investigate surface properties of the blends films, in order to find correlation between structural organization and surface composition and structuration, which are of prime interest in medical applications.

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