

MECHANICAL PROPERTIES OF POLY(VINYL CHLORIDE) - POLYMERIC PLASTICIZERS BLENDS

Claudia Tighiceanu¹

¹"Stefan cel Mare" University of Suceava, MANSiD Research Center, 13 University Street, 720229, Suceava, Romania, claudia.tighiceanu@usm.ro

Abstract: Poly(vinyl chloride) (PVC) is one of the most extensively used polymers because of its affordability, accessibility, and high compatibility with plasticizers. Plasticizers from the phthalate family are typically utilized in PVC, but they have negative effects on both human health and the environment, and they tend to leach out of the mixture. In this work, we evaluated the effect of macromolecular plasticizers, polycaprolactone and poly(ϵ -caprolactone)-*b*-poly(dimethylsiloxane), on the properties of PVC. The mechanical properties (Young's modulus, tensile strength and elongation at break) were evaluated. In general, the results have shown that both for the PVC/PCL mixture and for the PVC/PCL/PCL-*b*-PDMS mixture, the tensile behavior corresponds to PVC-based plasticized mixtures.

Keywords: Plasticizer, Polymer blend, Poly(vinyl chloride), Poly(ϵ -caprolactone), PCL-*b*-PDMS diblock copolymers

1. Introduction

One of the widely used polymeric material is poly(vinyl chloride) (PVC), with a huge commercial interest, due to low cost, accessibility to raw materials and to its properties. PVC is a linear, thermoplastic, predominately amorphous polymer [1]. To tailor its physical properties to various applications plasticizers are used in different amounts. Among them, phthalates are used due to their excellent properties as a plasticizer, their cost, convenience and adaptability [2-4]. Being low-molecular weight substances and not covalently bonded to the polymer, they can leach from the matrix, inducing harmful effects on human health and environment and a loss of plasticizing effect [5-7]. An efficient way to solve the problem is the use of polymeric plasticizers which present low volatility, high resistance to extraction and low migration at high temperatures [4,8]. One of the polymers reported to be an effective plasticizer for PVC is poly(ϵ -caprolactone) (PCL), the blends obtained having a better drape, softness and higher resistance to extraction by oil and water [8-10]. PCL is a hydrophobic polyester, biodegradable, semi-crystalline and with high toughness and biocompatibility, broadly used in biomedical

applications, especially for tissue engineering, drug carrier, drug delivery and scaffold for repairing tissue [11]. PVC is widely used for medical devices and part of them come in contact with blood (blood tubing for hemodialysis, intravenous solution dispersion system, catheters, cardiopulmonary bypass systems). Different polymers can be added to these blends to confer hemocompatibility. Among these, poly(dimethylsiloxanes) (PDMS) can be used, but they can provide only a temporary surface modification. PDMS are known to be incompatible with almost all organic based polymers and over a period of time this leads to their exudation from the system. An effective way to increase the compatibility is to form block copolymers of siloxanes with other polymers which are compatibles with the blends [12-13]. From the large variety of block copolymers synthesized up to now, those based on PCL and PDMS, the PCL-*b*-PDMS diblock copolymers, present a special interest because they insure a good combination between the properties of PCL (especially compatibility with many types of polymers) and PDMS (extremely low glass transition temperature, very high chain flexibility, hydrophobicity, biocompatibility, low surface energy, high lubricity). PCL segments act as "anchoring groups" for

siloxane blocks providing a permanent surface modification. [14,15].

In this work, polymer blends consisting of PVC, PCL and PCL-b-PDMS diblock copolymers with different molecular weights of the PCL block, were obtained and the mechanical properties of these blends were investigated. The objective of this experimental study was to determine how mechanical properties of PVC films are influenced by adding PCL and PCL-b-PDMS diblock copolymers as polymeric plasticizers.

2. Materials and methods

2.1. Materials

Poly(vinyl chloride) (PVC, $M_w=78000$ g/mol, Oltchim S.A., Ramnicu Valcea, Romania), poly(ϵ -caprolactone) (PCL, Fluka, $M_w=10000$), tetrahydrofuran (THF, 99%, Acros Organics) and bidistilled water were used as received. The poly(ϵ -caprolactone)-b-poly(dimethylsiloxane) (PCL-b-PDMS) diblock copolymers were prepared by anionic ring-opening polymerization of ϵ -caprolactone initiated from hydroxy-terminated PDMS. Molecular weight (M_n) of the diblock copolymers was determined by Proton Nuclear Magnetic Resonance (^1H NMR) and Size Exclusion Chromatography (SEC). Their characteristics are presented in Table 1 [16].

Table 1. Characteristics of PDMS-b-PCL diblock copolymers

PDMS-b-PCL diblock copolymer	A	B	C
M_n PCL ^a	700	5100	10,500
M_n PDMS ^a	4900	4900	4900
M_n copolymer ^a	5600	10,100	15,400
M_n copolymer ^b	6200	10,100	15,600
Polydispersity indices ^a	1.22	1.17	1.14
PCL content, wt%	12.5	51.48	68.18
PDMS content, wt%	87.5	48.52	31.82

^a Determined by ^1H NMR

^b Determined by SEC using a Polystyrene calibration curve

2.2. Polymer blends preparation

The polymer blends were prepared by solvent casting from THF with a total polymer blend concentration of 5 wt%. Required volumes of each component, calculated to obtain 3 mm thick films, were mixed together for 30 min with a magnetic stirrer. The solutions were poured into Teflon moulds (60 mm diameter), and THF was slowly evaporated under ambient conditions. The resulting films were dried in a vacuum oven for 72 h at 40°C.

Both binary PVC/PCL and ternary PVC/PCL/(PCL-b-PDMS) blends were prepared. In binary blends, the PCL content was 40 wt%. In ternary blends, the PVC content was kept constant (60 wt%) while varying the PCL and PCL-b-PDMS contents: part of the PCL (4, 12 and 20 wt%) was replaced with PCL-b-PDMS. Table 2 gives the real percentages of the different polymers (PVC, PCL, PDMS) present in the blends [14, 15].

Table 2. Composition of blends

Proba	PVC, %	PCL, %	PDMS, %
PVC	100	-	-
PVC-PCL	60	40	-
A-4	60	36,67	3,32
A-12	60	30,03	9,96
A-20	60	23,38	16,61
B-4	60	38,00	2,00
B-12	60	34,00	6,00
B-20	60	30,00	10,00
C-4	60	38,78	1,31
C-12	60	36,05	3,94
C-20	60	33,42	6,57

2.3 Mechanical testing

The mechanical properties of the prepared films was evaluated using a tensile testing machine with a set speed of 10 mm/min. (INSTRON 4605 G2).

3. Results and discussions

This work was based on the results obtained during Ph.D. thesis “Synthesis and characterization of block copolymers from heteromultifunctional initiators”, 2009, Iași, Gheorghe Asachi Technical University in cotutelle with Haute Alsace University, France.

The mechanical properties of plasticized and non-plasticized PVC films were determined to investigate the effect of the addition of plasticizer on their overall strength. The obtained data of Young modulus, tensile strength and elongation at break is presented in Table 3.

Table 3. Mechanical properties of films

	Young modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PVC	800	17	30
PVC-PCL	25	20	447
A-4	17	13	324
A-12	24	15	425
A-20	44	15	485
B-4	14	13	400
B-12	18	13	477
B-20	44	18	488
C-4	5	17	443
C-12	6	12	450
C-20	7	11	544

PVC film without plasticizer showed a Young's modulus of 800 MPa, a tensile strength of 17 MPa and an elongation at break of 30%. All plasticized PVC films showed a reduction of Young's modulus and an increase of elongation at break. This indicates that by replacing 40% of the PVC with a plasticizer, films with enhanced flexibility were obtained. The present results are consistent with previous reports, which also observed that the addition of plasticizer increases elongation at break [3,17,18].

Comparing the films that have similar composition, A-12 with B-20, B-12 with C-20, A-4 with C-12 and B-4 with C-4, it was observed that by increasing the molecular

weight of the PCL block elongation at break increases.

Increasing the percentage of diblock copolymer in blends have as results an increase in both Young's modulus and elongation at break of the analyzed PVC/PCL/PCL-b-PDMS films.

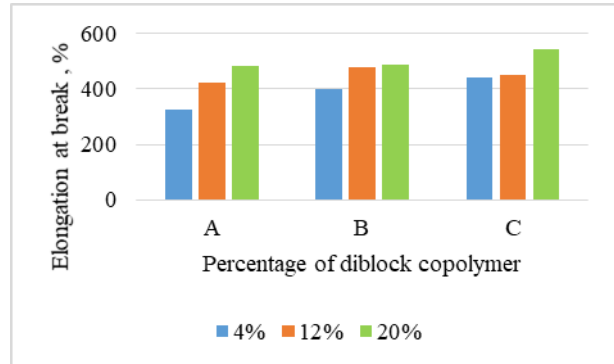


Figure 1. Influence of percentage of diblock copolymer on elongation at break of the blend

The tensile strength of the PVC/PCL/PCL-b-PDMS blends has values close to those of un-plasticized PVC and is not significantly influenced by the total PCL content of the blends.

4. Conclusions

PVC films plasticized with PCL or PCL/PCL-b-PDMS showed a reduction of Young's modulus and an increase of elongation at break. An increase of both Young's modulus and elongation at break was observed when the percentage of diblock copolymer was increased in the analyzed films. Mechanical testing of the prepared blends showed that both for the PVC/PCL mixture and for the PVC/PCL/PCL-b-PDMS mixture, the tensile behavior corresponds to PVC-based plasticized mixtures, making these potential plasticizers for PVC.

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