Macromol. Symp. ***176,*** *233–244 (2001)*

Modification of EVOH Copolymers with ε-Caprolactone: Synthesis and Compatibilization Effects in PE/PVC Blends

Maurizio Toselli[§]*, *Elena Fabbri*[#], *Paola Fabbri*[#], *Pierluigi Monari*[§],
Francesco Pilati[#], *Maria Pizzoli*[°], *Francesco Paolo La Mantia*[°°], *Roberto Scaffaro*[°°]

[§] Dipartimento di Chimica Applicata e Scienza dei Materiali, Università di Bologna,Viale Risorgimento 2, 40136 Bologna, Italy
[#] Dipartimento di Chimica, Università di Modena, Via Campi 183, 41100 Modena, Italy
[°] Dipartimento di Chimica, Università di Bologna, Via Selmi 2, 40127 Bologna, Italy
[°°] Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy

Summary: Polyethylene-polycaprolactone graft copolymers with different chemical structures (i.e. different number and length of PCL grafts and molecular weight of PE backbone) were synthesized from various EVOH copolymers and ε-caprolactone, using Aluminum isopropoxide as catalyst, and were tested for their compatibilizing capability in PE/PVC blends. PE and PCL segments in the graft copolymers were found completely immiscible, while PCL segments of the graft copolymers were found completely miscible with PVC. When graft copolymers were added to PE/PVC blends they proved to be good agents for the dispersion of PVC phase in the PE matrix. SEM showed also improved adhesion between the dispersed PVC phase and PE matrix. Moderate improvements in mechanical properties were also observed in preliminary tensile tests.

Introduction

In the last few decades, the most promising strategy for the preparation of new polymeric materials has been recognized in the blending of different polymers, and a large number of different blends have been considered 1). Theoretical and experimental studies demonstrated that most polymers are immiscible, leading to multiphase products on blending, and that a fine dispersion and a good adhesion at interface is a necessary condition for good mechanical properties of these blends. The particle dimension is mainly controlled by the viscosity ratio of the blended polymers, surface tension and mixing conditions, while a good interfacial adhesion requires suitable interactions between polymers at interface.

Theoretical studies 2) and experimental evidences 1,3-6) arrived at the conclusion that block and graft copolymers may behave as effective compatibilizers, by reducing surface tension and originating suitable interactions, when they are located (completely or in part) at the

CCC 1022-1360/00/$ 17.50+.50/0

interface. In this respect, the molecular structure of the copolymer (type, number and molecular weight of blocks or grafts and backbone) plays a key role; preferably, one type of segments should have a higher thermodynamic affinity for one of the blended polymers, whereas the other type of segments should have higher thermodynamic affinity for the other polymer of the blend. In this view, we undertook a study for the preparation of graft copolymers consisting of a PE backbone with PCL grafts. Such a type of copolymers should behave as compatibilizers towards several pairs of polymers such as polyethylene (PE) with PVC, but also polyolefins with polyesters or polycarbonates, etc. In fact, the PE segments of the copolymer is expected to have thermodynamic affinity for polyolefins, while PCL segments are miscible with PVC [1,7,8)], SAN [9)], and could undergo exchange reactions with various polycondensates such as polyesters, polycarbonates, polyammides. For this reason, these copolymers appear interesting additives for the compatibilisation of various blends, and in particular of PE and PVC blends, as well as for recycling purposes and for use as modifiers of PVC resins.

PE/PVC blends are inherently brittle, and several approaches have been proposed to improve their mechanical properties: co-crosslinking methods [10-12)], addition of rubber, chlorinated polyethylene [13)], PE-g-PVC or PE-g-PMMA graft copolymers [14)] and segmented EB-SAN copolymers [15)]. Aim of this study is the preparation of various PE-g-PCL copolymers, which in principle should be effective compatibilizers for PE/PVC blends, by reacting ethylene-vinyl alcohol copolymers (EVOH) with ε-caprolactone (CL). In particular EVOHs with different VOH contents and molecular weights were used, and different lengths of PCL grafts were obtained by changing the initial CL/EVOH reaction ratio. This paper describes also the thermal properties of these copolymers and some preliminary results of their effect on PE/PVC blends.

Experimental

Materials

EVOH with VOH content ranging from 3.1 to 6.7 mol% were obtained from hydrolysis of commercial EVA copolymers supplied by Polimeri Europa, with the characteristics reported in Table 1. CL monomer was purchased by Aldrich and distilled on CaH_2 under vacuum just before use. The catalyst, Aluminum isopropoxide (supplied by Aldrich), was usually distilled under vacuum before use; sometimes the procedure suggested from Duda [16)] was used to obtain an enrichment in the more active trimer form (A3). Reagent grade toluene was distilled before use after boiling on CaH_2, while methanol was used as received. PVC and PEs used for mechanical blending were commercial products: PVC was of K65 type addictivated with 2 wt% of calcium stearate as thermal stabilizer.

Copolymers Preparation and Characterization

Hydrolysis reactions of EVA were performed at 110 C in toluene solution (1:10 wt:vol) using $NaOCH_3$ in MeOH (30 wt%), with a 2:1 CH_3O^-/VA molar ratio. EVOH was dissolved in toluene (1-10% wt/vol) at about 110C and, after complete dissolution, the catalyst (from 2 to 0.1 wt% with respect to EVOH) was added; then CL monomer was added dropwise (within 10 min.) and was allowed to react under stirring for various times (10-30 h). Unreacted CL was separated from the graft copolymer by precipitation of the reaction solution in a large amount of methanol.

Table 1. Main characteristics of poly(ethylene-co-vinylacetate) and poly(ethylene-co-vinylalcohol) copolymers.

Sample code of EVA copolymers	MFI (g/10 min)	wt% of VA units	mol % of VA (or VOH) units	Sample code of EVOH copolymers
HX-50	150	18	6.7	HX-OH 50
CL-30	2.5	9.0	3.1	CL-OH 30
FF-35	0.7	9.0	3.1	FF-OH 35

Copolymers were characterized by FT-IR, H-NMR, GPC, DSC, DMA and TGA. FT-IR analysis was performed on a Bruker IFS48 instrument filming the copolymers from chloroform or toluene solution on a KBr disk. ^{1}H-NMR analysis was carried out on a Varian Gemini System 300 MHz instrument using $CDCl_3$ as a solvent at a temperature of 55C or C_2Cl_4/C_6D_6 (90/10) mixture at a temperature of 80C. GPC analysis was performed on samples soluble in chloroform using a set of PLgel columns 500, 10^3, 10^4 Å, chloroform as elution solvent at 0.8 mL/min and a RI detector. Selective extraction tests were carried out to separate the possibly formed PCL homopolymer from unreacted EVOH and/or grafted copolymers. Solubility of graft copolymers is affected by the content of VOH and molecular weight of the EVOH copolymer, and by the fraction of PCL grafted onto the PE backbone.

Preliminary tests showed that PCL homopolymer is readily soluble in cold chloroform, while EVOH and graft copolymers containing less than 30-40 wt% of grafted PCL are insoluble in cold chloroform. Therefore cold chloroform was typically used to separate the possibly formed PCL homopolymer from the products with a content of PCL lower than 30 wt% resulting from polymerization.

The instruments used for DSC, DMA and TGA were a DuPont 9900, a PL and a DuPont V5.1A 2000, respectively.

Blends Preparation and Characterization

Blends of PVC and graft copolymers were obtained from THF solution at about 55C. After solvent evaporation, films were then dried at 50C under vacuum before measurements. PE/PVC blends, with and without graft copolymers, were prepared in a Brabender internal mixer attached to a Brabender Plasticorder PLE 330. The mixing temperature was 180°C, the rotational speed 60 rpm, and the mixing time about 5 min (until constant torque was measured). The composition of the blends was either 80 wt% or 50 wt% of PE, and in the ternary blends from 2 to 10 wt% of the graft copolymer was added. The mechanical characterization was carried out on specimens derived from compression moulded sheets, with Instron machines. SEM micrographs were collected on a Philips XL-40 instrument equipped with SED e BSE detectors.

Results and Discussion

Graft copolymers with PCL grafted onto a polyolefin backbone have been barely described in the literature, and only as a new class of biodegradable polymers 17,18). In a recent paper it was reported the preparation of novel biodegradable polymers for drug release systems obtained by grafting PCL onto polyvinyl alcohol backbone 18). Previously, a patent claimed that PE-g-PCL graft copolymers showed good strength properties, similar or better than those of LLDPE, and improved biodegradability 17). Several different reactions were proposed for the preparation of these copolymers, including the reaction between EVOH and CL used in this work. However, in that patent only one type of EVOH was used for the preparation of PE-g-PCL copolymers, and the resulting products were poorly characterized 17).

The aim of this work is the preparation of various PE-g-PCL graft copolymers, with different chemical structures, to be used as compatibilizers in the blending of PE and PVC. Number and average length of the PCL grafts, and molecular weight of the PE backbone can play a relevant role in the compatibilizing efficiency, so that we carried out various reactions starting from commercial EVA with different vinyl acetate (VA) contents (and therefore with different average length of the PE segments between two grafts) and molecular weights. Indeed, VA groups in EVA are not suitable to start the ring-opening polymerization of CL, even in the presence of typical catalysts of ring opening polymerization, therefore, EVA samples were completely hydrolyzed in order to obtain EVOHs which contain hydroxyl groups that, in the presence of suitable catalysts, are able to start the ring-opening polymerization of CL.

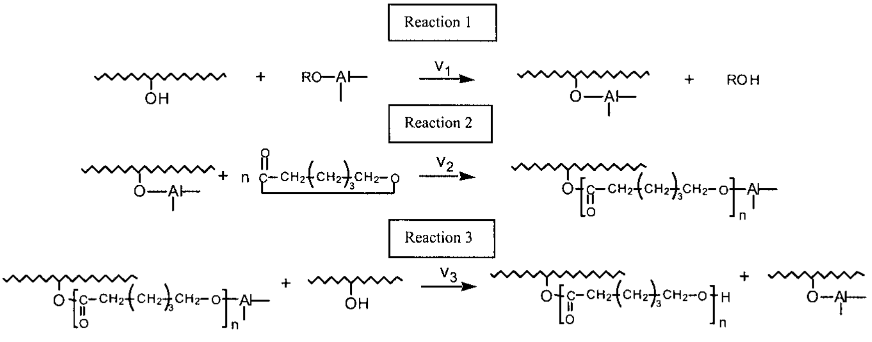

Figure 1. Reaction scheme of PE-g-PCL copolymers formation.

Aluminum isopropoxide, according to the recent literature [16)] the most convenient catalyst for the ring opening polymerization of CL (particularly in the more active trimer form, A3), was used to start CL polymerization. The reactions leading to the formation of PE-g-PCL copolymers are schematically reported in Figure 1.

Reaction 1) accounts for the reaction between –OH groups in EVOH and alcoxide groups of Aluminum isopropoxide; we observed a fast gelation occurring when Al(*i*-OR)$_3$ is added in suitable amount to EVOH; this suggest that this reaction occurs at a very fast rate under the used reaction conditions. The evidence, coming from selective extraction tests, that no PCL homopolymer was formed suggests that all Al(*i*-OR)$_3$ has reacted with EVOH. Furthermore, due to the excess of hydroxyl groups, Aluminum is probably attached, inter- or intramolecularly, to more than one VOH moiety. Reaction 2) accounts for the growth of PCL segments grafted onto EVOH, by insertion of CL monomer in the growing chains. Reaction 3) accounts for the exchange between –OH groups that were initially not reacted with Al(*i*-OR)$_3$ and PCL growing chains. The relative rate of reaction 3) with respect to reaction 2), determines the number of PCL grafts formed during polymerization. For $v_3 \gg v_2$ all the -OH groups of EVOH would be involved in the formation of PCL grafts, while when $v_3 \ll v_2$ PCL grafts would grow only on -OH groups which underwent reaction 1)

The mechanism is therefore much more complex than it can appear from Figure 1, and there is need of more studies in order to determine the relative rates of reactions 2) and 3).

Information about the content of PCL in the graft copolymers were obtained by several techniques: namely, ^{1}H-NMR, FT-IR and TGA. The PCL weight percentage of graft PE-g-CL copolymers calculated from NMR and FT-IR analyis are reported in Table 2 and 3. The same PCL composition was also confirmed by thermogravimetric analysis (TGA).

Table 2. Composition of PE-g-PCL copolymers.

Code of graft copolymers	Code of used EVOH	wt% of PCL in the copolymer	CL/VOH (mol/mol)
HX-CL(74)	HX-OH 50	74	10
HX-CL(82)	HX-OH 50	82	17
HX-CL(86)	HX-OH 50	86	23
CL-CL(24)	CL-OH 30	24	2-3
CL-CL(58)	CL-OH 30	58	11
CL-CL(77)	CL-OH 30	77	27
CL-CL(86)	CL-OH 30	86	48
FF-CL(39)	FF-OH 35	39	5
FF-CL(55)	FF-OH 35	55	10
FF-CL(70)	FF-OH 35	70	18
FF-CL(80)	FF-OH 35	80	32
FF-CL(85)	FF-OH 35	85	44

Table 3. Structure of PE-g-PCL graft copolymers from EVOH HX-OH 50 (*).

Reaction time (h)	Conversion CL (%)	wt% of PCL in the copolymer	CL/VOH (mol/mol)	average number of CL units	% of reacted OH
4	34	22	1.0	5	17
5	41	27	1.4	7.4	18
6	50	33	1.8	8.3	21
8	67	45	3.0	11.7	25
14	94	62	6.0	17	32

(*) Reactants ratio: EVOH/CL/toluene/cat. = 1/2/70/0.02 (wt/wt/vol/wt).

Selective extraction tests and GPC curves showed that no PCL homopolymer was formed during polymerization, and therefore all PCL present in the final product is grafted onto PE backbones. For example, in Figure 2, GPC curves are reported of polymeric products of the reaction between EVA (a) or EVOH (b) and CL at different reaction times, using the same initial EVA copolymer (full line on the graph) for comparison. It is possible to note that the amount of PCL in the polymer products deriving from EVA/CL reaction, that is PCL homopolymer, increases when the reaction time is increased, but the maximum values of MWD are always at higher retention volumes (lower molecular weights) with respect to the initial EVA polymer. On the contrary, when reaction is performed starting from EVOH, those values are shifted at lower retention volumes, for degrees of CL conversion similar to those of Figure 2(a). This last result, together with the absence of a second peak at higher retention volumes, is a further support to hypothesis that all of PCL chains are grafted onto PE backbones.

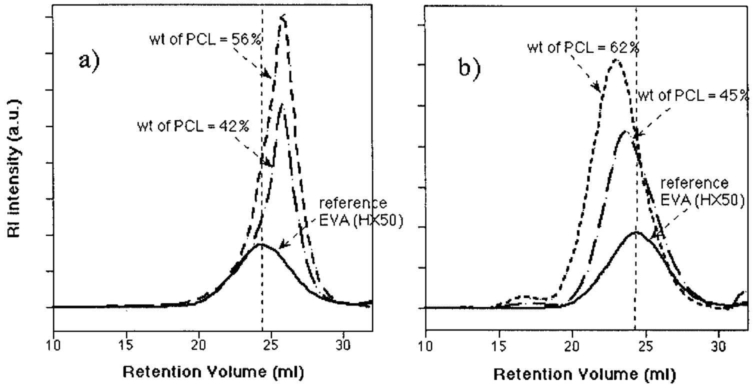

Figure 2. GPC curves of polymeric products of: (a) EVA/CL and (b) EVOH/CL reactions.

The average length of PCL grafts may be of great importance for the correlation between molecular structure of the copolymer and its final effect as compatibilizer. Assuming that all –OH groups are involved in the formation of PCL grafts, the average polymerization degree of the PCL grafts can be easily estimated by the CL/VOH molar ratio in the copolymer; these data are reported in Table 2 and 3. However this may be an apparent average length which could differ from the actual average length. If PCL chains grow only on a fraction of the -OH groups, the real average length of PCL grafts would be higher than that calculated from the CL/VOH ratio.

Indeed, preliminary results, obtained just for one kind of EVOH, showed that the OH groups involved in the polymerization are only a fraction, ranging from 17 to 32% of the overall amount (Table 3). More details about the synthesis and the molecular characterization of these graft copolymers will be reported in another paper in preparation.

DSC and DMTA were used to investigate the thermal behavior of the graft copolymers, and hence to derive information about the miscibility of PE and PCL segments in the copolymers.

Typical DSC curves are reported in Figure 3 for samples derived from the same initial EVOH (FF-OH 35), but with different contents of PCL.

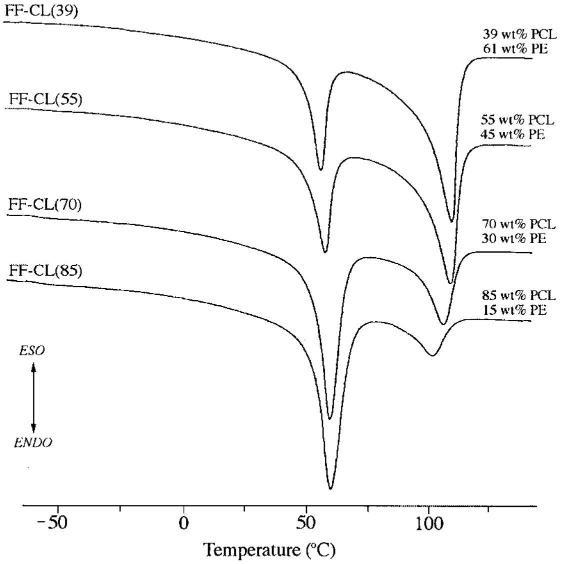

Figure 3. DSC curves of PCL-g-PE copolymers derived from EVOH FF-OH 35.

As it appears, two melting peaks are present, one attributable to the melting of PCL crystallites (at about 60°C), the second to PE crystallites (from 110 to 102°C, for PCL content increasing from 39 to 85 wt% respectively). For both peaks ΔH_m changes linearly with composition. It is interesting to compare T_m and ΔH_m of the graft copolymers with those of the EVA from which they are derived. It results that the presence of long PCL segments leads to higher T_m and H_m than those found for the parent EVA. Therefore we can conclude that PCL segments do not limit the crystallization capability of the PE segments, but, on the contrary, they seem to favour nucleation and growth of PE crystallites with respect to the corresponding EVA.

DMTA spectra of the graft copolymers are in complete agreement with the DSC results; they didn't show any appreciable change in the position of T_g of the PCL phase (at -50C) and of the typical transition of PE segments (at -120°C) in EVOH samples. The intensity of these transitions increased with the increase of PCL and PE content, respectively.

From these data we can conclude that PE and PCL segments of the graft copolymers are completely immiscible, regardless of the chemical structure of the copolymer.

Thermal characterization of blends of PVC with PE-g-PCL copolymers

Blends of PVC with PCL homopolymer (m.w. 2000) and with graft copolymers with different lengths of PCL segments were prepared from THF solutions (PVC content from 90 to 70 wt%). As expected from literature data [8], DSC curves recorded from PVC/PCL blends showed a single T_g intermediate between those of PVC and PCL. Some typical DSC curves for blends of PVC with PE-g-PCL copolymer are reported in Figure 4.

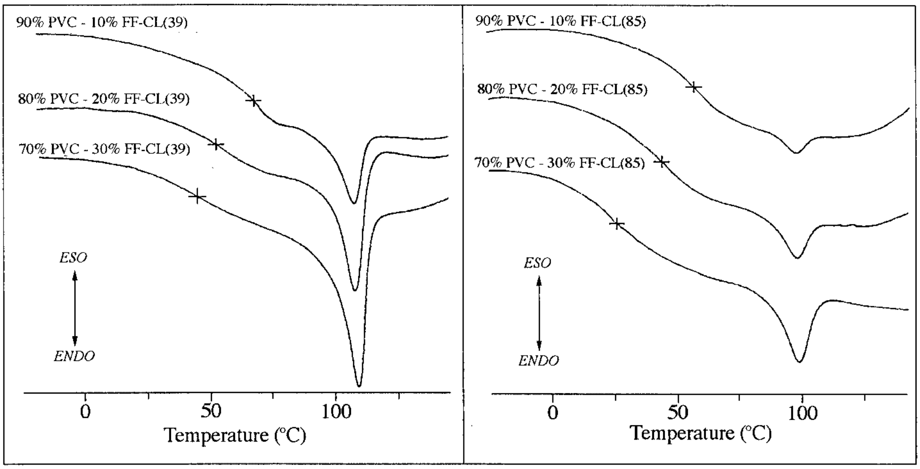

Figure 4. DSC curves of PVC- graft copolymer [FF-CL(39) and FF-CL(85)] blends.

As it appears the melting peak of PCL crystals is absent and a single T_g, which decreases as the content of PCL increases, is present. The values of T_g of the blends correspond to those expected for complete miscibility of the PCL segments with PVC, in fact the T_gs obtained from blends of PVC and PCL homopolymers and the T_gs of blends of PVC and graft copolymers are described by the same curve in a plot of T_g against the PCL content in the PVC+PCL amorphous phase. A melting peak attributable to a PE phase is also detectable in the DSC curves; as expected for a separated PE phase, T_m was the same of the pure graft copolymer and did not change with the blend composition, while ΔH_m increased with increasing the PE content in the overall blend.

From these data it is possible to conclude that the PCL segments of the graft copolymers behave like PCL homopolymer with respect to PVC, being able to undergo complete mixing with PVC, while the PE backbone of the graft copolymer appears completely immiscible in the PVC+PCL phase and separates in a distinct phase.

Effect of graft copolymers on blends PE/PVC

Some preliminary studies of the compatibilizing effect of the various graft copolymers in ternary blends with PE and PVC were carried out by SEM and mechanical testing.

Two typical SEM micrographs of PE/PVC (80/20) blends (with and without copolymer added), prepared in a internal mixer and fractured in liquid nitrogen, are reported in Figure 5.

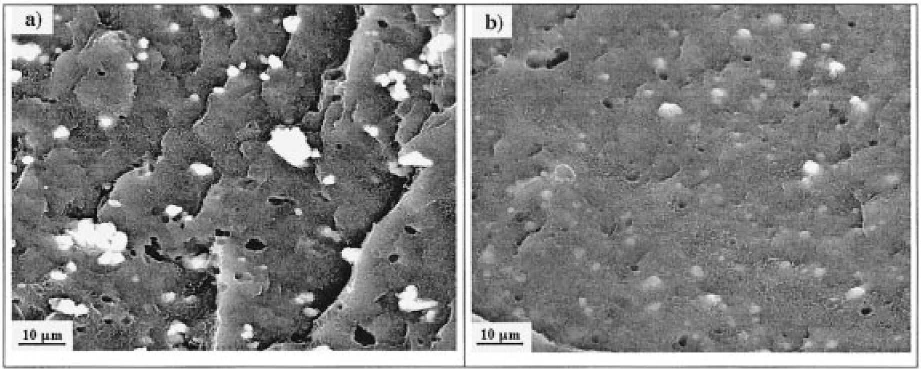

Figure 5. SEM micrographs (1000x) of PE/PVC (80/20) blends: a) without copolymer added, b) with 5% of CL-CL(86) copolymer.

As it appears, a finer dispersion of PVC was obtained when 5 wt% of the graft copolymer CL-CL(86) was added to the PE/PVC blend, suggesting that it plays a relevant role in the control of the final morphology of the blend. When the same amount of graft copolymer with different chemical structure [CL-CL(24), CL-CL(58), HX-CL(82) and FF-CL(80)] was added to the blend, changes in morphology similar to those previously described in Figure 5 were observed. This suggests that the length of PCL segments, the molecular weight of the PE backbone, and the length of the PE segment between two grafts have a limited effect on morphology. Micrographs of samples containing graft copolymers recorded at higher magnification (20000x), showed also a very good adhesion of the PVC particles to the matrix.

Tensile tests were also carried out on blends with and without graft copolymers added. No attempts to optimize the mixing conditions were made, and therefore the results, obtained under the same conditions, have to be considered just for comparison rather than as the best values possible for the ternary blends. Most tests were carried out on PE/PVC 80/20 blends and the results are reported in Table 4.

Table 4. Tensile tests of PE/PVC blends with and without graft copolymers added.

PE/PVC wt/wt ratio	Used copolymer code	wt%	Stress at break (MPa)	Elongation at break (%)
80/20	----	----	17.9 (±0.6)	5.6 (±0.6)
80/20	HX-CL(82)	2%	19.4(±0.3)	6.2 (±0.3)
80/20	HX-CL(82)	5%	18.2(±0.4)	5.5 (±0.8)
80/20	CL-CL(24)	2%	18.3 (±0.2)	6.5 (±0.8)
80/20	CL-CL(24)	5%	18.0 (±0.2)	6.2 (±0.4)
80/20	CL-CL (86)	2%	20.0(±0.4)	6.0 (±0.5)
80/20	CL-CL (86)	5%	19.3(±0.3)	5.1 (±0.4)
80/20	FF-CL(80)	2%	19.3(±0.5)	4.4 (±0.5)
80/20	FF-CL(80)	5%	19.5(±0.3)	5.9 (±0.4)
80/20	FF-CL(80)	10%	19.0(±0.5)	5.1 (±0.7)

As expected, the binary PE/PVC blend shows a brittle behavior and poor mechanical properties because of the incompatibility of the two components. Most of the ternary blends, containing 2, 5 or 10 wt% of different graft copolymers, show a moderate improvement of stress and elongation at break, even though the increase of the mechanical properties are relatively small. The small difference in mechanical properties observed for various samples (with different amount and type of copolymers) does not allow to derive definite conclusions as regard to the effect of amount and chemical structure of PE-g-PCL copolymers on compatibilisation.

A few other tests were carried out on the more brittle 50/50 blends and the results are summarized in Figure 6; as it appears, the effect of the length of the PCL segments in the graft copolymer is more evident, and the blend with CL-CL(86), which contains 86 wt% of PCL, shows a significant improvement of strength and elongation at break with respect to the simple PE/PVC control sample and to the blends containing graft copolymers with shorter PCL grafts.

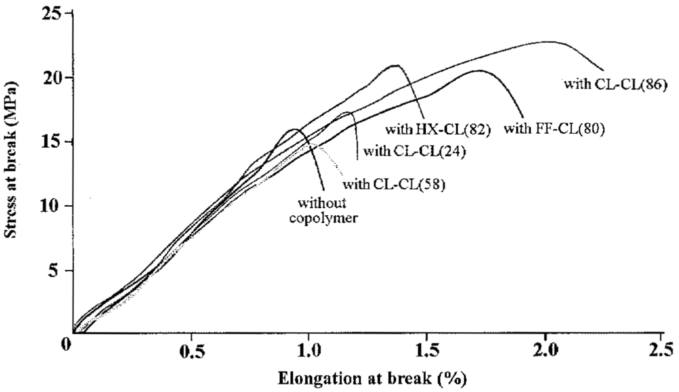

Figure 6. Tensile curves of PE/PVC blends with and without graft copolymer added (5 wt%).

References

1. L.A. Utracki, in: Polymer Alloys and Blends, Hanser Publisher, New York 1989.
2. J. Noolandi and K.M. Hong, *Macromolecules*, **15**, 482 (1982); J. Noolandi and K.M. Hong, *Polym. Bull.*, 7, 561 (1982); J. Noolandi, *Polym. Eng. Sci.*, **24**, 70 (1984).
3. D. Heikens, N. Hoen, W. Barentsen, P. Piet and H. Ladan, *J. Polym. Sci. Polym. Symp.*, **62**, 309 (1978).
4. D.R. Paul and S. Newman (Eds.), *Polymer Blends*, Academic Press, New York, 1978.
5. D.W. Fox and R.B. Allen, *"Compatibility", in Encyclopedia of Polymer Science & Engineering*, Wiley, New York, 1985, vol. 3.
6. C. Koning, M. Van Duin, C. Pagnoulle and R. Jerome. *Prog. Polym. Sci.*, **23**, 707 (1998).
7. R.E. Prud'homme, *Polym. Eng. Sci.*, **22**, 90 (1982).
8. T.P. Russel and R.S. Stein, *J. Polym. Sci., Polym. Phys.*, **20**, 1593 (1982); T.P. Russel and R.S. Stein, *J. Polym. Sci., Polym. Phys.*, **21**, 999 (1983);
9. P.B. Rim and J.P. Runt, *Macromolecules*, **16**, 762 (1983).
10. W.J. McGill, J. Fourie, *J. Appl. Polym. Sci.*, **19**, 879 (1975).
11. Y. Nakamura, A. Watanabe, K. Mori, K. Tamura, H. Miyazaka, *J. Polym. Sci., Polym. Lett. Edn*, **25**, *127 (1987)*.
12. Y. Nakamura, A. Watanabe, K. Mori, K. Tamura, M. Inagaki, *J. Mater. Sci.*, **21**, *4485 (1986)*.
13. A Ghaffar, C. Sadrmohaghegh, G. Scott, *Eur. Polym. J.*, **17**, 941 (1981).
14. B. Boutevin, Y. Pietrasanta, M. Taha, T. Sarraf, Polym. Bull., **14**, 25 (1985).
15. E. Kroeze, G. den Brinke, G. Hadziioannou, *Polymer*, **38**, 379 (1997).
16. A. Duda, S. Penczek, *Macromol. Rapid Commun.*, **16**, 67 (1995).
17. F.C. Schwab, US patent, US5321088 (1994).
18. A. Breitenbach and T. Kissel, *Polymer*, **39**, 3261 (1998)