Polymer Bulletin 14, 25–30 (1985)

Polymer Bulletin

Influence of Graft Copolymers P (E-g-MMA) on the Mechanical Properties of PE-PVC Alloys

Bernard Boutevin, Yves Piétrasanta, Mohammed Taha, and Tarek Sarraf

Laboratoire de Chimie Appliquée, Ecole Nationale Supérieure de Chimie, 8, rue Ecole Normale,
F-34075 Montpellier Cedex, France

ABSTRACT

The emulsifying effect of P(E-g-MMA) copolymers is examined on PE/PVC mixtures. With added quantities of copolymers varying between 2.5 to 5.0%, the breaking strenght values σ_B are found to be almost double that of homopolymer mixtures. Copolymer emulsifying properties are observed in the fractographs of these polymer alloys analysed under a scanning electron microscope. A comparison with other copolymers used as emulsifiers on the same mixtures is made.

INTRODUCTION

Polymer alloy preparation and optimization constitute an interesting line of research with a view to improving the use and recuperation of common polymers. We are interested here in mixtures of low density polyethylene (LDPE) and polyvinylchloride (PVC). Because of their great incompatibility, the best way to improve the mixture mechanical properties consists in adding an emulsifier common to the two aforesaid polymers, which would provoke a closer binding of these polymers. Several authors have written about the coupling which interest us.

First, chlorinated polyethylene containing 35% to 50% chlorine can be used as an additive (LOCKE et al, 1973). In this case, the additive contains elements of the two initial polymers. In most cases, the polyethylene sequence is kept in the emulsifier, while the PVC portion is replaced by a sequence easily miscible with PVC. For example, this sequence can be constituted with ε-caprolactone (HEUSCHEN, 1977). Other authors have shown that polymethylmethacrylate (PMMA) is also partially miscible with PVC (SCHURER et al, 1975), especially in the adhesive synthesis for raw rubber and PVC (PENDLE, 1973).

These experiments have been compiled in "Polymer Blends" (PAUL, 1978). As far as our previous experimentation is concerned, we prepared copolymer, LDPE grafted by PMMA (BOUTEVIN et al, 1984). Their use as an emulsifier for LDPE/PVC mixtures is discussed below.

RESULTS AND DISCUSSION

P(E-g-MMA) copolymers are prepared by ozonisation of LDPE (LOTRENE, CDF CHIMIE, FI 20) and the grafting of MMA in bulk onto the hydroperoxide thus obtained. The proportionate mass of PMMA to that of PE is 26%. The specific mass of the PVC used is of 136 g/cm^3.

The LDPE/PVC/P(E-g-MMA) mixtures are made on a roller-mixer at 190°C. Tensile bars (standard iso 1/2), cut out of the moulded sheets, are then tested on an INSTRON tensile apparatus with a speed of 2 cm/mn. A minimum of 4 tensile bars is tested for each mixture and the averages are retained. First of all, using a LDPE/PVC mixture, 50/50 by weight, we sought the optimum quantity of P(E-g-MMA) necessary to obtain the best breaking strain σ_B. The results are shown in Table I.

TABLE I - σ_B variation versus P(E-g-MMA), (%)

The ratio of added copolymer (%) to 100% mixture	σ_B(Kg/mm²)
0	0.60
2.5	1.10
5	1.25
10	1.27
15	1.26

Note that, from 5% upwards of copolymers, σ_B does not increase and remains at 1.25 kg/mm². This value was chosen for studying various mixtures.

The mechanical characteristics of this P(E-g-MMA) copolymer were measured under the same conditions as the PE/PVC mixtures. The results are the following :

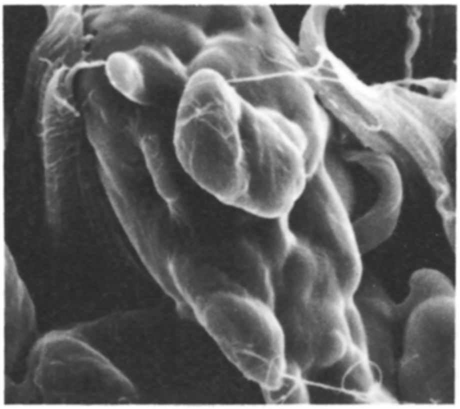
$$\sigma_B = 0.89 \text{ kg/mm}^2$$
$$\varepsilon_B \text{ (\%)} = 4.4\%$$
$$E = 27.6 \text{ kg/mm}^2$$

Secondly, σ_B values were established for several LDPE/PVC mixtures of variable proportions (see Table II).

TABLE II - Effect of a 5% addition of graft copolymer P(E-g-MMA) on LDPE/PVC mixture breaking strain σ_B

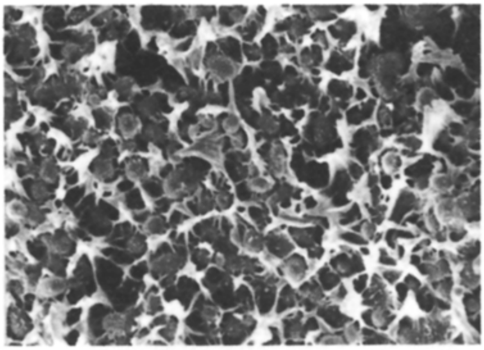
mixture composition		modulus E_2 (kg/mm²)		σ_B (kg/mm²)		elongation at breaking point E_B	
PE	PVC	without copo.	with copo.	without	with	without	with
100	0	9.72	9.11	0.80	0.81	238	220
80	20	12.6	12.8	0.64	0.84	54.2	52
60	40	13.4	21.1	0.62	0.96	28.4	15.4
50	50	24.3	28.1	0.60	1.10	15.5	10.4
40	60	30.9	39.5	0.67	1.18	9.3	5.3
20	80	50.3	61.5	1.27	1.67	3.4	6.3
0	100	106.5	112	4.92	4.64	7.6	6.12

Rupture at room temperature. PE/PVC mixture (50/50) after mixing for 4mn at 190°C

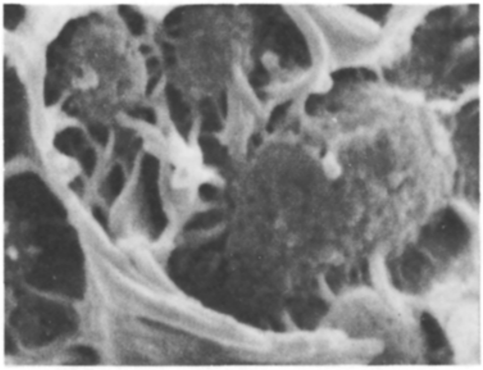


1cm=5μ

PE/PVC/COPO(E-g-MMA) mixture (50/50/5).



1cm=5μ



1cm=1μ

The modulus E(Kg/mm²) is seen to increase by up to 30% with an addition of the copolymer in mixtures of around 50/50. In mixtures of these proportions, σ_B is also seen to increase very significantly, almost by 100%. Thus, for the LDPE/PVC mixture (50/50), without emulsifier, a σ_B value of 0.60 kg/mm² is obtained, whereas when 5% P(E-g-MMA) copolymer is added, σ_B is 1.10 kg/mm².

The elongation at breaking point is less when the LDPE content is superior to 30% and greater below that.

Therefore, it should be noted that the mechanical properties of the high PVC content mixtures are clearly improved and that the use of the proposed emulsifier leads to a real alloy.

The alloy fractographs were also examined under the scanning electron microscope. Without copolymer, in the LDPE/PVC mixture 50/50 for example, we observed PE nodules of 30μ in average diameter (Figure 1). On the other hand, in the same mixture with an addition of 5% copolymer, the average diameter of the nodules is less than 2μ (Figure 2). In this last case, when the magnification is increased, the presence of adhesions between the two phases is observed (Figure 3).

This underlines the emulsifying role played by the copolymer.

It is interesting to compare our results with those of other teams.

First of all, when chlorinated LDPE is used as an additive (LOCKE et al. 1973), in LDPE/PVC, 50/50 mixtures, σ_B is seen to be almost constant, whereas ε_B increases significantly. For this, 10 to 40% chlorinated PE is added however. What is more, it appears that the least chlorinated additive is the most efficient.

As for the PE-polycaprolactone copolymer - $\overline{M}n$, 60.000 and 80.000 respectively - used as an additive (TEYSIE, P. et al. 1981), the mixture σ_B are not changed by this component and the authors even point out that it generally causes a substancial decrease of ε_B, so as to throw doubt on the efficiency of this emulsifier.

In conclusion, the P(E-g-MMA) copolymer that we prepared, can be considered as a suitable emulsifier for LDPE/PVC mixtures.

Moreover, it presents the advantage of being more accessible for industrial synthesis than block copolymers obtained by an anionic process.

REFERENCES

LOCKE C.E., PAUL,D.R. and VINSON,C.E. : Polym.Eng.Sci.,13, 202 (1973).
LOCKE C.E., and PAUL, D.R. : Polym.Eng.Sci,13, 308 (1973).
HEUSCHEN, J., Thèse de doctorat - Université de Liège (1977).
SCHURER, J.W., de BOER A., and CHALLA G. : Polymer, 16,201 (1975).
PENDLE, T.D., in "Block and Graft copolimerization" (CERESA, R.J., ed.),Vol.1,p.83, WILEY, New-York,1973.
PAUL, D.R., and SEYMOUR NEWMAN, in "Polymer Blends", PAUL, D.R.,Vol.2, Chep.12,p.35, ACADEMIC PRESS,New York,1978.
BOUTEVIN,B., PIETRASANTA,Y., SARRAF,T., and TAHA, M.: Europ. Polym. J. 20,1131 (1984).
TEYSSIE, P., FREDERIX,H., FAYT,R., and GILINQUET,A. : "Comportement industriel des alliages polymériques. Analyse et perspectives nouvelles". C.R.I.F.,Registration N° in the Bibliothèque Royale D/1981/0567/6.BRUXELLES.

Accepted July 9, 1985

C