PET/R-PP/PC Blends by Two-stage Reactive Extrusion: Effect of Polypropylene Reactively Functionalized with an Oxazoline Group on Morphology and Mechanical Properties

Regina Jeziórska

Industrial Chemistry Research Institute, Rydygiera 8 st, 01-793 Warsaw, Poland

Summary: A series of PET/R-PP/PC blends was studied in a chemical modification involving reactive extrusion with a ricinyl-2-oxazoline maleinate. The interfacial reaction between blend components were studied by the differential scanning calorimetry (DSC) and the scanning electron microscopy (SEM). The static tensile and flexural properties, and impact resistance response of the blends were tested. The phase morphology of the blends was of interpenetrating network (IPN) type according to SEM results. The blends offer excellent mechanical properties and improved impact strength as an effect of chemical reactions on reactive extrusion, even if PET waste and low PC contents (below 20%) have been used.

Introduction

The increasing use of poly(ethylene terephthalate) (PET) bottles results in an increasing amount of secondary PET waste which should be recycled in a cost-efficient manner. The main problem faced during processing of recycled PET is degradation resulting from the simultaneous presence of retained moisture and contaminants. Such contaminants, i.e., poly(vinyl chloride) (PVC) and adhesives generate acidic compounds at processing temperatures, catalyzing hydrolytic ester bonds cleavage, leading to lower molecular weights and higher amount of carboxylic end groups[1-2]. The major application of the secondary PET is, however, still fiber spinning and strapping, where a reduced molecular weight is tolerated[3]. Our intention was to convert the PET waste into thermoplastic polymers of high-impact strength using low-cost reactive extrusion. In this case polymers are reacted through their functional groups while being processed, and the processing equipment such as a twin-screw extruder or mixer acts as a mini reactor[4-5]. Block copolymers formed during reactive extrusion, as a result of interchain exchange reactions, play a role of compatibilizers.

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

The overall objectives of this work were to functionalize a PP homopolymer with a ricinyl-2-oxazoline maleinate (ROM) *via* melt grafting process and to evaluate the effectiveness of oxazoline grafted PP (R-PP) on the structure and properties of PET/R-PP/PC blends.

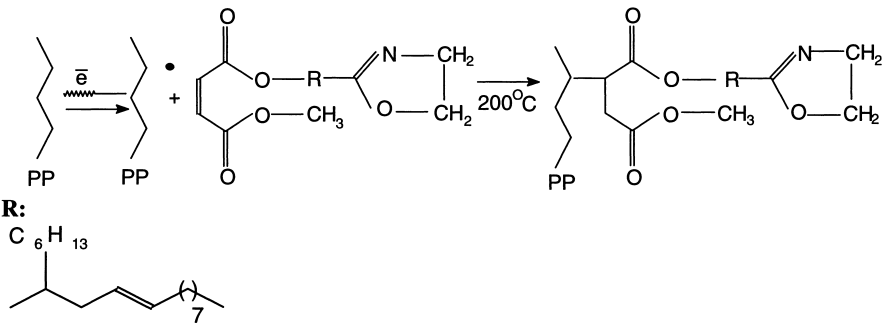
Experimental

Polypropylene (PP) was commercial product supplied by Polski Koncern Naftowy SA, Poland. Polycarbonate (PC) (intrinsic viscosity = 0.61 dlg^{-1} in 1,1,2,2-tetrachloroethane/phenol, 50/50 wt/wt, at 25^0C) was purchased from Bayer, Germany. PET waste flakes (intrinsic viscosity 0.65 dlg^{-1} in the same solvent at 25^0C) was supplied by Customer, Poland (Table 1). Ricinyl-2-oxazoline maleinate was obtained from Henkel, Germany. Before using, PC and PET flakes were dried under vacuum at 120^0C, while PP was dried at 80^0C.

Table 1. PET scrap characteristic.

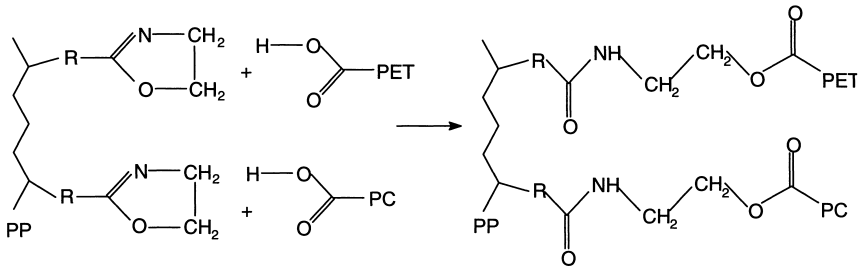
Property	Value
Dimension	
> 8 mm, < 0.6 mm	< 1 %, < 0.5 %
Metal content	< 3 ppm
Paper content	< 10 ppm
PVC content	< 25 ppm
HDPE content	< 25 ppm
Sugar content	< 10 ppm
Humidity	< 0.02 %

Procedure



Reaction 1

Reactive extrusion of reactive PET/R-PP/PC blends was performed in a pilot-plant "Berstorff" twin-screw extruder (D = 25 mm, L/D = 33) as a two-stage process [6-7]. At stage I, PP and ROM were melted at 180 – 200^{0}C and the modified PP was irradiated with a fast-electron beam (Reaction 1); at stage II, PP reactively functionalized with an oxazoline group (R-PP) was coupled together with PET waste and PC at 245 – 270^{0}C (Reaction 2). The residence time of the reactants was 3 minutes, respectively.



Reaction 2

Testing methods

Differential scanning calorimeter (DSC) was performed on a Perkin-Elmer (DSC-2) apparatus. The process was carried out in a triple cycle „heating-cooling-heating" in the temperatures ranges 0 to 250^{0}C. The rate of heating and cooling was 10^{0}C min^{-1}. The glass transition temperature (T_g) was determined from the temperature diagrams as the temperature corresponding to the upper inflection point or maximum of the curve. The melting point (T_m) and crystallization temperature (T_c) were determined as corresponding to the maximum of the endothermic curve and the minimum of the exothermic curve, respectively.

Solubility tests of the samples were carried out in a Soxlet apparatus with methylene chloride for 48h.

Selective degradation of the PC fraction in the PET/R-PP/PC blends was performed with piperidine in methylene chloride.

The intrinsic viscosity of PET/R-PP segments after selective degradation of PC segments was calculated from viscosity measurements of diluted solutions in 1,1,2,2-tetrachloroethane/phenol (50/50 wt/wt) at 25^{0}C using Ubblehode viscometers.

The morphology of the fracture surface of the specimens was studied *via* scanning electron microscope JSM 6100, Jeol. Samples were fractured under liquid nitrogen after 3 min and then vacuum coated with gold.

The melt flow index (MFI) was examined by plastometer type II RT according to standard PN-93/C-89069 (ISO 1133/1991), at 270^{0}C.

The tensile data were collected at room temperature with an Instron 4505 tensile tester at a crosshead speed of 5 mm/min.

The flexural data were collected at room temperature with a Zwick apparatus.

Results and discussion

According to DSC data presented in Table 2, the two-stage process results in formation of heterophasic blends with a single glass transition temperature (T_g) and improved enthalpy. Crystallization and melting temperatures of the R-PP phase in the PET/R-PP/PC blends do not essentially change. However the values of T_c and T_m of the PET phase increase. The enhanced values of T_c, result in higher stability of the product. Crystallization heat of PET fraction is increased while the ΔH_c of R-PP fraction is decreased. This together indicates, indirectly, that specific interactions have occurred in the blends on reactive extrusion.

Table 2. Thermal properties of PET/R-PP/PC.

PET/R-PP/PC	T_g (^{0}C)	T_{m1} (ΔH_{m1}) (^{0}C) (J/g)	T_{c1} (ΔH_{c1}) (^{0}C) (J/g)	T_{m2} (ΔH_{m2}) (^{0}C) (J/g)	T_{c2} (ΔH_{c2}) (^{0}C) (J/g)
100/0/0	82	-	-	148, **250** (44.4)	161 (30.0)
75/15/10	90	155, **164** (125.3)	118 (86.7)	258 (49.2)	201 (44.0)
70/20/10	92	150, **164** (105.4)	119 (79.0)	258 (48.8)	202 (48.4)
65/20/15	87	150, **165** (124.8)	117 (93.3)	258 (48.8)	199 (44.1)
60/25/15	92	159, **164** (115.6)	118 (89.7)	257 (47.8)	199 (45.3)
0/100/0	-	62, **164** (89.2)	112 (98.8)	-	-
0/0/100	146	-	-	-	-

Data of solubility of the resulting blends in methylene chloride can be used for qualitative evaluation of the final polymer composition. The values obtained for the soluble fractions of the non-reactive blends in methylene chloride correspond exactly to the PC weight fraction (Fig. 1, 2), which indicates the absence of chemical interactions in the polymer system during extrusion. The solubility of the reactive blends decreases significantly and confirms a formation of block copolymers. This fact indicates that the interfacial reaction occurs during

reactive extrusion, which results in a reduction of the initial content of the non-reacted PC fraction.

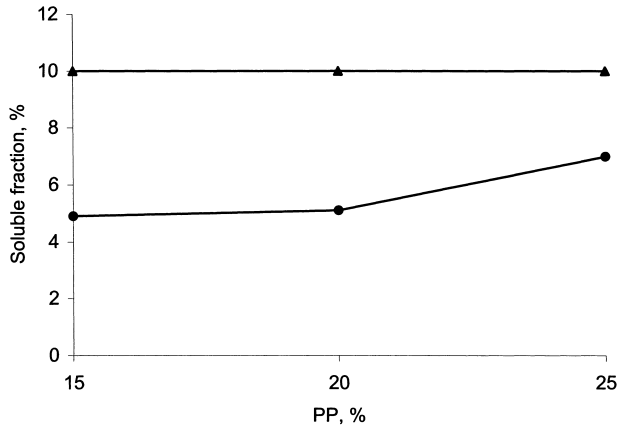


Fig. 1: Solubility data for PET/R-PP/PC blends as a function of PP content;
● = reactive blend, ▲ = non-reactive blend

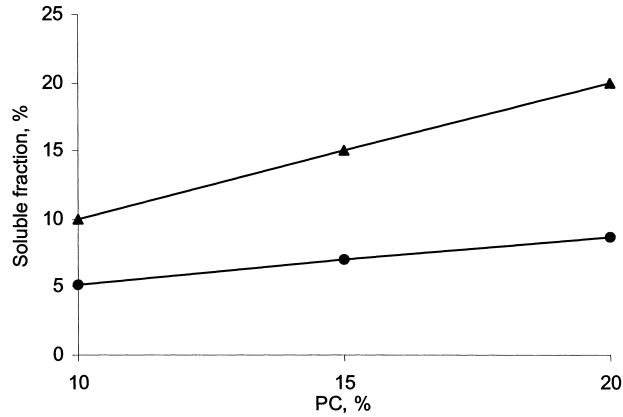


Fig. 2: Solubility data for PET/R-PP/PC blends as a function of PC content;
● = reactive blend, ▲ = non-reactive blend

The method of selective degradation of PC moieties in PET/R-PP/PC blends with piperidine allows to evaluate the length of residual PET/R-PP segments. The improved values of the intrinsic viscosity of the residual PET/R-PP segments in the reactive blends indicate the

formation of block copolymers with the PET blocks gradually extended with an increase in the R-PP and PC content (Fig. 3). The observed fast increase of the viscosity of PET/R-PP segments can be mainly attributed to exchange reactions rather than degradation.

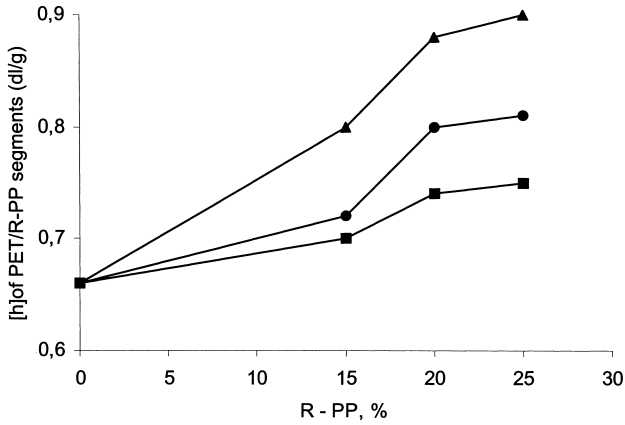


Fig. 3: Intrinsic viscosity data for PET/R-PP segments after selective degradation of the PC fraction in the PET/R-PP/PC blends; ■ = 10% PC, ● = 15% PC, ▲ = 20% PC

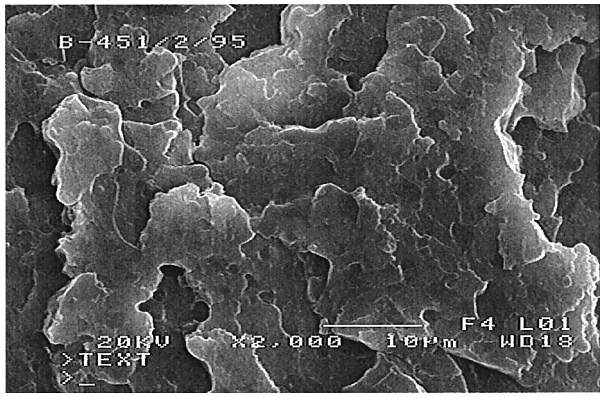


Fig. 4: SEM micrograph of PET/R-PP/PC (60/25/15)

PET/R-PP/PC samples were also examined by a SEM technique. Phase structure studies showed that interfacial reactions between R-PP functionalized with an oxazoline group and PET and PC having co-reactive groups are effective in the compatibilization of investigated

blends. Thus, the micrograph of the fractured surface of the sample presented in Figure 4 demonstrates a compatible heterophasic character of interpenetrating network (IPN) type. All this suggests that there is very good adhesion between the phases as a result of intermolecular reactions.

Improvement in impact properties is the most important reason for blending. Table 3 lists properties of the reactive PET/R-PP/PC blends. The impact improvement initially increases with R-PP and PC. Oxazoline functionality results in toughening the blends accompanied by a slight decrease of flexural strength and modulus. The MFI of the blends dramatically decreased. This fact indicates substantial amounts of interfacial reaction and molecular weight increase.

As seen in the Table 3, the reactive blends offer excellent mechanical properties as an effect of chemical reactions on reactive extrusion, even if PET scrap and low PC contents have been used.

Table 3. Properties of PET/R-PP/PC.

PET/R-PP/PC	σ_g/MPa	E_g/MPa	σ_r/MPa	ε_r/%	a_u/kJ/m^2	a_n/kJ/m^2	HDT/^{0}C	MFI/g/10min
100/0/0	86	3200	41	1.6	11	1.6	70	14.5
75/15/10	76	2600	50	5.3	> 100*	7.2	77	0.3
70/20/10	73	2520	54	7.6	> 100*	7.8	78	0.2
65/20/15	71	2470	56	8.8	> 100*	9.4	76	0.2
60/25/15	66	2310	58	9.4	> 100*	9.7	75	0.2

σ_g = flexural stress, E_g = flexural modulus, σ_r = tensile stress at break, ε_r = strain at break, a_u = impact (Charpy) at 23 °C , a_n = impact (notched) Charpy at 23 °C, HDT = high deflection temperature under load 1.8 MPa, MFI = Melt Flow Index (270^{0}C, 1.2 kg, die I),
* the samples (4 x 10 mm) have not been broken under impact of energy 4J.

Conclusions

It has been shown that the interfacial reactions between polypropylene reactively functionalized with an oxazoline group and PET and PC having co-reactive groups are effective in the compatibilization of the polymer blends. The graft copolymer formed on the reactive extrusion results in an alloy with good interfacial adhesion. The presented method of PET/R-PP/PC reactive extrusion by two-stage process provides a possibility to produce a variety of new polymer materials with a single T_g by varying the concentration of R-PP and initial polymer composition.

References

[1] G. Giannotta, R. Po, N. Cardi, E. Tampellini, E. Occhiello, F. Garbassi, *Polymer Engineering and Science, Mid-August*, **34**, 1219 (1994)
[2] N. Cardi, R. Po, G. Giannotta, E. Occhiello, F. Garbassi, G. Messina, *Journal of Applied Polymer Science*, **50**, 1501 (1993)
[3] J. Milgrom, *Plastics Recycling* (Ed.:J. Ehring), Hanser Publishers, Munich 1992, p. 45
[4] H. Inata, S. Matsumura, *Journal of Applied Polymer Science*, **32**, 5193 (1986)
[5] W. E. Baker, M. Saleem, *Polymer*, **28**, 2057 (1987)
[6] R. Jeziorska, W. Zielinski, Z. Roslaniec, J. Słonecki, *Polimery,* **44**, 38 (1999)
[7] R. Jeziorska, W. Zielinski, *ICRI Ann. Rep. 99*, 42 (1999)