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Filled Grades of Chemically Modified Poly(ethylene terephthalate)

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SUMMARY: Structural phases and blends properties of glass fiber filled reactive PET/R-PE blends (85/15 and 75/25 wt/wt) were studied in a chemical modification involving reactive extrusion with a ricinyl-2-oxazoline maleate. The present method offers compatible heterogenous blends with the structure stabilized at microphase level and with advantageous macroscopic properties, *viz.,* impact and tensile resistance, processability. The most important effects of glass fiber reinforcement are increases in strength (tensile and flexural) and stiffness (flexural modulus).

Introduction

Recently more attention has been focused on reactive polymer processing, in which superior polymer alloys are produced during melt processing. In this case polymers are reacted through their functional groups while being processed, and the processing equipment such as a twin-extruder or mixer acts as a mini reactor [1-3].

Poly(ethylene terephalate) (PET) is well known as commercially important polymeric material. Although PET shows good toughness and ductility in unnotched tests, sharp notches effectively decrease the impact strength. This limitation has led to intensive and successful efforts to modify the polyester with elastomers. Examples include the modification of PET with amorphous thermoplastics and with PBT. There have been additional successful developments, especially in filled products.

This paper presents the study on the morphology and mechanical properties of glass fiber filled products of reactive PET/R-PE blends that have been obtained by

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a chemical modification involving reactive extrusion with a ricinyl-2-oxazoline maleate (ROM).

Experimental

Low density polyethylene (PE) used in these studies was obtained from the Polski Koncern Naftowy SA, Poland. Fiber-grade PET (intrinsic viscosity 0.65 dlg^{-1} in phenol/1, 2-dichlorobenzene, 50/50 (wt/wt) at 25^{0}C) was commercial product of the Elana SA, Poland. Ricinyl-2-oxazoline maleate was obtained from Henkel, Germany. Aminosilane coated cut glass fiber (3 mm long) was supplied by the Vetrotex, France.

Procedure

Reactive extrusion of the filled grades of reactive PET/R-PE blends, using weight ratios of 85/15 and 75/25, was performed in a pilot-plant “Berstorff” twin-screw extruder (D = 25 mm, L/D = 33) as two-stage process 4-6). At stage I, ROM was melt grafted onto a low density polyethylene at 180 – 200^{0}C using a peroxide initiator; at stage II, PE reactively functionalized with an oxazoline group (R-PE) was coupled with PET at 235 – 270^{0}C. Glass fiber, at a concentration of 15 or 25 wt %, was added to the reaction mix at 15D length down the barrel. The residence time of the reactants was 3 minutes.

Results and Discussion

To establish the structure of polymers mixtures, it is necessary to apply several methods. In this study, structural evaluations were based on dynamic mechanical thermal analyses (DMTA), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC).

In Figure 1 the DMTA traces of the glass fiber filled reactive PET/R-PE blend (85/15 wt/wt) plotted as a function of temperature show relaxation processes to occur during the transition from the glassy state to the polymer melt. The storage modulus (log E') indicates an insignificant decrease of E' values near the T_g. After T_g, the E'-values decrease monotonically but slightly up to the melting point and rapidly past the melting point. Both the loss modulus and the loss tangent (tan δ) show double maximums. The first maximum (relaxation β) near -50°C results from molecules disturbances in a crystalline phase and chain ends disturbances. The second maximum (relaxation α) near 100°C refers to the glass transition of the PET amorphous phase. However, DMTA thermograms show no peaks of PE relaxation.

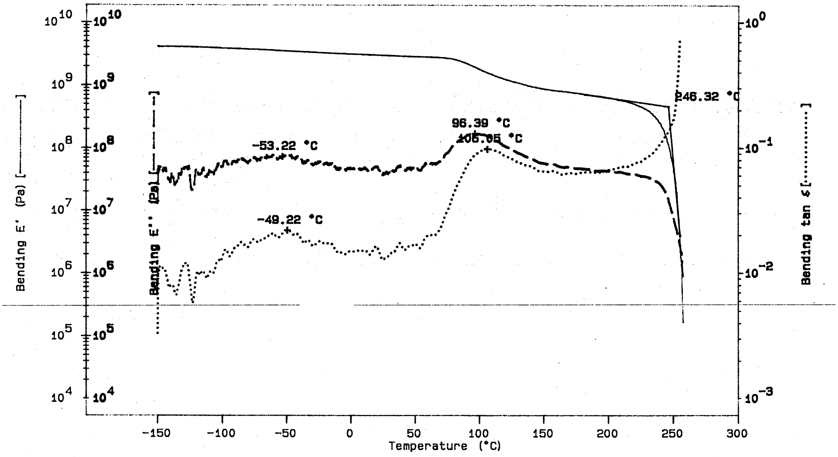

Fig. 1:. The storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) of a reactive PET/R-PE blend (85/15) with 25% of glass fiber:

PET/R-PE samples were also examined by a SEM technique. As representative examples micrographs of blend 85/15 with 15% of glass fiber and blend 75/25 with 25% of glass fiber were presented in Fig 2 and 3, respectively. Phase structure studies showed that interfacial reactions between R-PE functionalized with an oxazoline group and PET having co-reactive groups are effective in the compatibilization of the blends. Thus, the micrographs of the fractured surface of the glass fiber filled samples presented in Fig. 2 and 3 demonstrate a compatible structure with continuous and interpenetrated phases of R-PE and PET. All this suggests that there is very good adhesion between the two phases, and it is a result of intermolecular reactions between the two polymers.

The effectiveness of glass fiber reinforcement is based essentially on the transfer of the load from the matrix to the fiber via the interface. The filled grades of the reactive PET/R-PE blends are characterized by strong interfacial adhesion between the fiber and the matrix (Fig. 2 and 3).

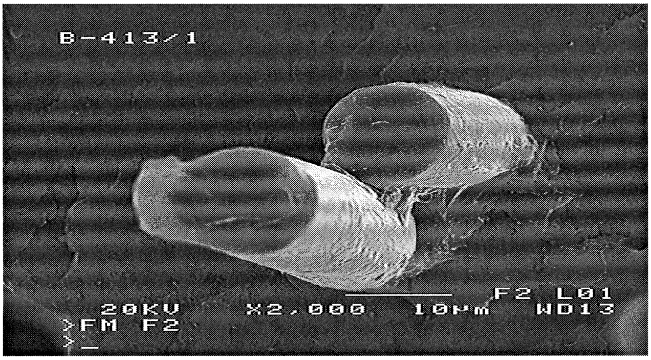

Fig. 2:. SEM micrograph of PET/PE blend 85/15 with 15% of glass fiber.

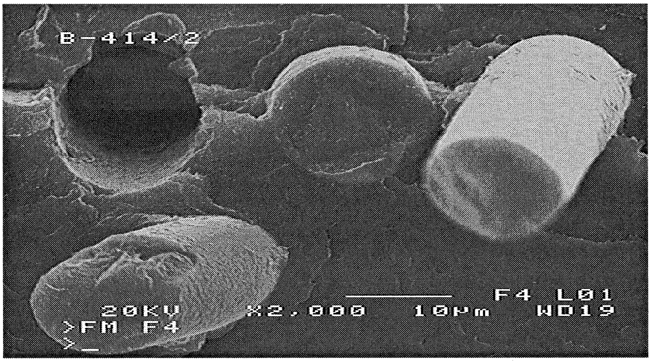

Fig. 3: SEM micrograph of PET/PE blend 75/25 with 25% of glass fiber.

According to DSC data presented in Table 1, melting temperature of the PET phase in the filled reactive PET/R-PE blends do not change. The values of the transition temperature T_g were lower (74^{0}C) for filled products than for the pure PET (88^{0}C). This together with disappearance of the T_g in the reactive PET/R-PE blends indicates, indirectly, that interfacial reactions have occurred on reactive extrusion. For the filled reactive PET/R-PE blends the values of the glass transition temperature slightly decrease for the samples with higher glass fiber content.

Table 1. Properties of PET, reactive PET/R-PE blends with glass fiber.

Property	PET	85/15			75/25		
		Glass fiber, wt %					
		0	15	25	0	15	25
Stress at break, MPa	41	53	98	109	46	82	102
Strain at break, %	1.6	3.7	3.2	2.8	4.9	2.6	3.3
Flexural stress, MPa	93	70	144	165	56	127	156
Flexural modulus, MPa	3340	2530	5430	7500	2040	5160	6980
Tensile creep modulus, MPa	3050	2300	5100	7200	1800	4800	6700
Charpy impact strength, kJ/m^2							
- notched	1.9	6.8	5.9	8.9	7.8	5.8	8.6
- unnotched	11.0	82.8	21.3	26.9	nb	21.5	32.1
Glass transition temperature, ^{0}C	88	-	80	74	-	79	74
Melting temperature, ^{0}C	259	261	258	258	260	259	259
Deflection temp. (1.8 MPa), ^{0}C	80	89	152	180	88	150	179
Humidity absorption, %	0.4	0.3	0.2	0.2	0.25	0.15	0.15
Melt Flow Rate, g/10min (270^{0}C, 1.2 kg, die I)	5.1	2.0	1.2	0.8	1.5	1.0	0.5

nb - no break

Improvement in impact properties is the most important reason for blending. Table 1 lists properties of the reactive PET/R-PE blends as R-PE and glass fiber concentration. In the reactive PET/R-PE blends the impact improvement initially increases as the functionalized PE concentration in the PET matrix is raised, to attempt a maximum of higher concentrations. It appears that, when the oxazoline concentration is high, the R-PE particles are too small to terminate cracks during impact. Although the impact strength increases, mechanical properties, particularly flexural strength and stiffness are compromised. For each application there is an optimum compromise.

As compared with the unfilled, the filled grades have better tensile and flexural strength. The most important effects of glass fiber reinforcement is the increase in stiffness (flexural modulus). In addition, creep resistance, and notched impact strength are increased, whereas elongation is decreased. With constant glass fiber reinforcement, the increase in impact strength with increasing R-PE content is minimal (Tab. 1). Additional advantages resulting from glass fiber are better dimensional stability, due to reduced mold shrinkage and less water absorption.

Filled reactive PET/R-PE blends have very good thermal resistance, particularly against thermal shock. The heat distortion temperature is influenced by the increased stiffness.

The melt flow rates of filed blends decreased progressively from 2.0 g/10 min to 0.5 g/10 min as the percentages of R-PE and glass fiber were increased. The decrease of the melt flow rate may well be caused by a change in intermolecular forces or increased molecular weight, particularly when high matrix phase oxazoline are used.

Conclusions

It has been shown that the interfacial reactions between polyethylene reactively functionalized with an oxazoline group and PET having co-reactive groups are effective in the compatibilization of the polymer blends.

The most important effects of glass fiber reinforcement of chemically modified fiber-grade PET are increased in strength (tensile and flexural) and stiffness (flexural modulus).

References

1. H. Inata, S. Matsumura, *Journal of Applied Polymer Science*, **32**, 5193 (1986).
2. W. E. Baker, M. Saleem, *Polymer*, **28**, 2057 (1987).
3. N. Cardi, R. Po, G. Giannotta, E. Occhiello, F. Garbassi, G. Messina, *Journal of Applied Polymer Science*, **50,** 1501 (1993).
4. *Pol. Pat. Appl.* P-314409 (1996).
5. R. Jeziorska, W. Zielinski, Z. Roslaniec, J. Słonecki, *Polimery,* **44**, 38 (1999).
6. R. Jeziorska, W. Zielinski, *ICRI Ann. Rep.'99*, 42 (1999).