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Study of morphological and mechanical properties of PP/PBT blends

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Summary : The synthesis of emulsifiers has been performed by the condensation of terephthaloyl chloride, butanediol and hydrogenated α–ω hydroxy polyisoprenes. The products are carefully characterized by ^{1}H-nuclear magnetic resonance (NMR), infra-red spectroscopy and size exclusion chromatography.

The PP/PBT blend, in a 60:40 ratio, was prepared with, and without, emulsifiers by melt-blending. The effect of these emulsifiers on mechanical properties and morphological studies of the PP/PBT blend was examined.

INTRODUCTION

The study of polymer blends has been the subject of numerous works of scientists over recent years (1-4).

Polymer blending is a means of producing new materials having a wide range of properties. In theory, the mixing of polymers is more economically viable than the synthesis of new ones. However, the majority of polymer blends are immiscible, confering to materials possessing poor mechanical properties (5-11). The phases are not linked to each other by any physical or chemical links.

It is possible to compatibilize immiscible blends by adding a third polymer, called a compatibilizer, that would reduce one particle size of the dispersed phase and promote interactions across the matrix-dispersed phase interface (12,13).

This emulsifier is generally constituted of a block copolymer (14-17) where each block is compatible with one of the components of the blend.

For example, some emulsifiers have been studied in order to compatibilize polyalkyl terephthalate/polyolefin blends (18-23).

Barlow and coll (24) used 5 % by weight of a triblock copolymer of styrene-ethylene butene1-styrene to compatibilize a PET/PE blend in a 50:50 ratio. This addition leads to a elongation at break of 35 % instead of 5 % without the prepared emulsifier. Other copolymers, such as graft copolymers prepared in situ, have been used. R. Parsy and coll (25) noted a morphological evolution of PBT/PS blends when they added 1 % of PP containing 6,6 % of maleic anhydride (AM). The sizes of modules decrease from 14 mm to 5 mm by the use of emulsifier. In the case of PBT/PS blend, the addition of 1 % of PS containing 8 % of AM leads to phase sizes of 6,4 mm instead of 37 mm for PS/PBT blend.

More recently, copolymers having ionic groups, called ionomers, have been used as compatibilizers in situ. Indeed, Maiti and coll (26-27) exhibited that the addition of poly(ethylene-co-sodium methacrylate) on PEhd/PBT in a 80:20 ratio increased the breaking strength by 25 % and decreased the elongation at breack.

On the other hand, Japon patents used graft copolymers in the PS/PBT blends (28,29). For example, Tsuda and coll (30) synthesized a graft copolymer PBT-g-PS. The addition of 10 % of this emulsifier in the PBT/PS (in 80:20 and 60:40 ratios), affected neither the elongation at break nor the breacking strength ; but the impact strength increased by 100 %.

The object of this study is to determine the compatibilizing effect of a hydrogenated polyisoprene, modified by segments of polybutylene terephthalate, on the morphology and mechanical properties of PP/PBT in a 60:40 ratio.

EXPERIMENTAL PART

A - Synthesis of emulsifiers

A-1 - Materials

Terephthaloyl chloride, butanediol and all solvents were reagent grade products and were used as supplied by Aldrich.

Toluene was kept over sodium for 24 hours and pyridine was freshly distilled. Hydrogenated α–ω hydroxy polyisoprenes were obtained from Atochem and used without further treatment. They have the following specifications :

- molecular weights : Mn = 11000 and 5000 g/mol
- functionality : 0,6
- polydispersity : 1,6
- microstructure exhibits :
  of 1,4 - units and of 1,2 - units

A-2 - Syntheses of emulsifiers

The emulsifiers were prepared by condensation of the terephthaloyl chloride, butanediol and hydrogenated α–ω hydroxy polyisoprene in 20:20:1 molar ratio. The reactions were carried out in the usual two step ways.

In the first step, in a three-necked round-bottom flask (equipped with a magnetic stirrer, a thermometer and a dropping funnel) were introduced 0,002 mole of hydrogenated α–ω hydroxy polyisoprene and 0,08 mole of pyridine in toluene. 0,04 mole of terephthaloyl chloride in anhydrous toluene was added. Stirring was performed for 48 hours at 110° C.

In the second one, 0,04 mole of butanediol was added, and the temperature was maintained for 48 hours. After reaction, the homopolymer of PBT and pyridinium chloride were separated from the reaction mixture by filtration.
The pure emulsifier was obtained by precipitation in acetone.

A-3 - Characterization

Structure of the emulsifiers was determined by ^{1}H-nuclear magnetic resonance (NMR), infra-red spectroscopy (FTIR), and size exclusion chromatography (SEC).

^{1}H-NMR spectra were recorded on a Brucker AC 200 apparatus using deuterated chloroform as both internal reference and solvent.

FTIR spectra were obtained with a Nicolet apparatus. The accuracy of the bands was given with an error of +/- 2 cm^{-1}

SEC investigations were monitored with a waters Associates Apparatus equiped with microstyragel columns ; the diameters of the pores were 10000, 1000, 500 and 100 Å respectively.

The detection was performed by a refractometer model BD 40.Tetrahydrofuran (THF) was used as the eluent (flow 1.5 ml/mn at 27°C).

B - Blend and mechanical tests

The blends were prepared using a Brabender cell kneader at 250°C. The twinning speed of the rollers was 48 rpm. The materials coming from the mixer were molded with a heated compression press, at a temperature of 250°C and a pressure of 20 bars. The specimens were tested with a Instron 1195. A crosshead speed of 2 mm/mn was needed to measure the breaking strength and elongation at break.

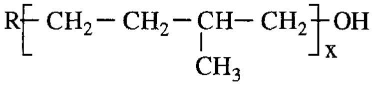
SEM (scanning electron microscopy) was used to analyse surface fractures. The test bar was cooled in liquid nitrogen and then broken. The surface was observed by SEM with a Cambridge Stereoscan 100.

RESULTS AND DISCUSSION

A - Syntheses of emulsifiers

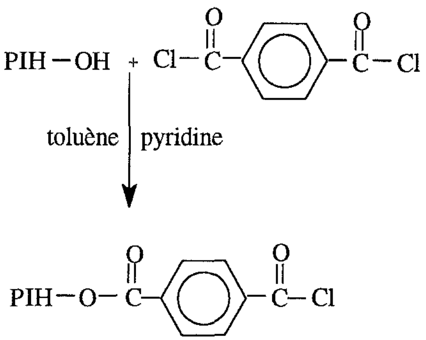
The emulsifiers were prepared from the hydrogenated α–ω hydroxy polyisoprene (PIH-OH), since it has a similar structure to that of PP. This polymer presents the next structure :

PIH–OH :

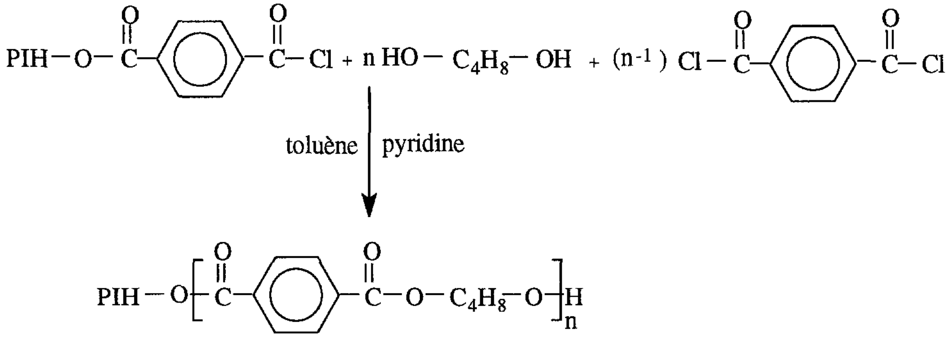


$$R\left[CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2 \right]_x OH$$

and it has been synthesized by Atochem using an anionic method. We used two polymers of 5000 and 11000 g/mol and the index of polydispersity is 1,6 and the functional group content is 0,6. The syntheses of the emulsifiers (the hydrogenated polyisoprenes modified by segments of butyleneterephthalate), are carried out by condensation, in two steps. The first step is the activation of PIH-OH with an excess of the terephthaloyl chloride, according to the following scheme :



The reaction was performed for 48 hours at 110°C. Second step is the condensation of the butanediol and the terephthaloyl chloride with the activated PIH-OH, as represented by the following scheme :



The reaction was performed under the same conditions as above. The PBT homopolymer and pyridinium chloride were separated from the mixture by filtration, and the emulsifier was isolated by precipitation in acetone. The purification has been controled by SEC. The ^{1}H-NMR spectra of the product (fig. 1) shows the expected signals of the protons of PBT incorporated in emulsifier. The protons of the methylene group in position a about the ester group are shifted at 4.4 ppm. A singlet is observed at 2 ppm which corresponds to methylenic protons located in the b position of the ester group. The chemical shift at 8.1 ppm is characteristic of aromatic protons.

Finally, FTIR analysis indicates the presence of the ester group band at 1718 cm^{-1}.

The PBT content in the emulsifier was calculated by measuring the areas of the aromatic protons and those of the hydrogenated polyisoprene protons. The contents are confirmed by elemental analysis of C, H and O elements. The results are summarized in Table 1.

Emulsifiers	% PBT by ^{1}H-NMR	% PBT by elemental analysis
emulsifier 5000	5,3	5,6
emulsifier 11000	1,4	1,7

Table 1 : PBT content in the emulsifiers.

We observed that the PBT content in the emulsifier is increased when the molar weight of hydrogenated α–ω hydroxy polyisoprene is reduced.

B - Study of PP/PBT blends

Upon utilisation of SEM on PP/PBT blends (60:40 weight ratio) without any emulsifiers, one obtains the following result :

The resultent blend is incompatible, and contains PBT modules (particle size 138 mm) inserted in a continuous phase (PP). A significant reduction in the module size and an increasing of the dispersion phase are evident when 5 % of the emulsifiers have been added (Tab 2). These results are in agreament with the litterature, concerning the effect of emulsifiers in blends (31-35).

We observed an improvement of the interface adhesion when emulsifier 5000 is used (fig. 3). This can be explained by the fact that the emulsifier 5000 is richer in PBT than the emulsifier 11000. So, the anchorage of the copolymer in the PBT modules is better and leads to a better adhesion interface.

PP/PBT blend	Adhesion	Dispersion	Particle size (um)	Figure
without emulsifier	poor	poor	138	2
with emulsifier 5000	good	medium	-	3
with emulsifier 11000	poor	good	14	4

Table 2 : Characteristics of PP/PBT blend

Stress strain tests were performed at room temperature at 2 mm/mn crosshead speed. Maximum stress and elongation at break were recorded.

The results were based on ten samples of PP/PBT (60:40) blends and blends containing 5 % of emulsifier. The results are summarized in Table 3.

PP/PBT blend	Breaking strength (MPa)	Elongation at break (%)
without emulsifier	17,2	3,3
with emulsifier 5000	10,5	14,1
with emulsifier 11000	12	2,7

Table 3 : Mechanical tests of blends with and without emulsifiers

In all cases, the addition of the emulsifier in the PP/PBT blend reduces the maximum stress level. For emulsifier 5000, we note that elongation at break increases by a noticible amount, from 3,3 % to 14,1 %. In the case of emulsifier 11000, the elongation is not notably modified while breaking strength decreases. The anchorage of the emulsifier 11000 in the blend seems to be insufficient to improve the mechanical properties of the blend.

CONCLUSION

The syntheses of the emulsifiers have been investigated by condensation in solution of hydrogenated α–ω hydroxy polyisoprene with the PBT precursors. The content of PBT in the emulsifier increases when the molar weight of the hydrogenated α–ω hydroxy polyisoprene decreases. The effect of these emulsifiers has been studied in PP/PBT blends. Thus, the incorporation of 5 % of the emulsifiers induces a reduction of particle size of PBT dispersed in the continuous phase of PP. A good adhesion is observed for emulsifier 5000. This adhesion results in a notable increase of the elongation at break (14,1 % instead of 3,3 %)

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