

Multifunctional coupling agents. Part 4: Block copolymers based on amino terminated polyamide-12 and carboxy terminated poly(butylene terephthalate)

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Abstract

A carboxy terminated poly(butylene terephthalate) (PBT) was obtained by quantitative reaction of a hydroxy terminated PBT with succinic anhydride. Subsequent melt mixing with an amino group terminated PA12 did not result in the formation of linking groups between the components. Instead, the formation of succinimide terminal groups on the polyamide-12 (PA12) chains was observed.

The same conversion in presence of a bifunctional coupling agent possessing one oxazoline and one oxazinone group yielded PA12/PBT block copolymers in high extent. DSC and microscopic measurements showed that a phase separated morphology is predominant.

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1. Introduction

During the last decades, mixtures of different polycondensates such as polyamides, polyesters, and polycarbonates have attracted big interest from both the scientific and industrial point of view. The inherent ability of polycondensates to undergo exchange reactions facilitates compatibilization when polycondensates are used as components in polymer blends. A comprehensive monograph concerning trans-reactions in condensation polymers was given by Fakirov [1]. These trans-reactions comprise reactions between the linking groups in the backbone of the polycondensates as well as reactions of the terminal groups.

The trans-reactions in mixtures of polyesters and polycarbonates are well established. Several products have been commercialized which benefit from this kind of compatibilization. From the application point of view, mixtures of crystalline

polyesters (PET, PTT, PBT) with crystalline polyamides (PA6, PA66, PA12) are less common. Yet, some new approaches have shown that such mixtures also have some prospective applications making them objects of intense research. Fakirov et al. [2–4] indicated that in mixtures of polyesters and polyamides microfibrils of the polyester were formed during processing. These microfibrils are assumed to reinforce the mixtures. Trans-reactions between the fibrils and the matrix ensured good adhesion between the components. Other useful applications of polyamide/polyester resins are imaginable in fields where material properties such as rheological behaviour, crystallinity, water uptake and hydrolytic stability of a thermoplastic have to be tuned. In the patent literature, the necessity of good adhesion at the phase boundaries of polyamide/polyester laminates was pointed out [5–7]. Here, compatibilized polyamide/polyester mixtures may act as adhesives.

Although utilization of trans-reactions seems to be very attractive, some drawbacks have also to be mentioned. In order to achieve sufficiently high conversion rates, trans-reactions demand high reaction times, and temperatures and have to be catalyzed. For polyamides/polyester blends *p*-toluene

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sulfonic acid (TsOH) was frequently used as catalyst. Recently, it was shown by Samperi et al. [8] that TsOH reacts with the polyester to form carboxylic groups which react quickly with the polyester phase. In other words, the role of TsOH is not that of a catalyst but of a reactant. It is obvious that this reaction is accompanied by chain degradation which influences mechanical properties. Additionally, condensation steps occurring during the trans-reactions form by-products which have to be removed carefully from the mixture. To overcome these problems, compatibilization of polyamide/polyester blends has been performed with polyaddition type coupling agents.

Bifunctional coupling agents such as bisoxazolines [9,10], bisoxazinones [11], bisoxazolones [12], diisocyanates [13], bisepoxides [14], and bislactamates [15–17] have found broad application in polymer modification and reactive processing. They have proved to be effective chain extenders for various polycondensates and reactive compatibilizers in polymer blends. To promote coupling reactions between the components of polyamide/polyester laminates bisoxazoline derivatives were used [6]. Nery et al. [18] describe the preparation of statistical multi-block copolymers based on dicarboxy terminated polyamides and polyesters by using various arylene bisoxazolines. The highest reactivity was observed when 2,2'-(2,6-pyridylene)bis(2-oxazoline) was used as coupling agent. In another example, a multifunctional epoxy resin was used as compatibilizer for PA6/PBT blends [19].

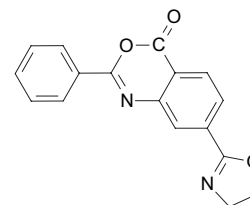
The application of coupling agents with two reactive groups of the same type as mentioned above is limited to polymers and blends containing the same type of reactive groups. For polyesters, which usually contain carboxylic groups, bis-2-oxazolines can be used. Hydroxy and amino groups rather react with bis-2-oxazinones or bislactamates. In the case of polymers containing different reactive groups, a combination of coupling agents was applied [15].

The situation in polymer blends is more complicated. The use of coupling agents with reactive groups of the same type causes reactions not only in the interface but also in the individual phases. If the coupling agent is more soluble in one of

the blend components, the latter can even become predominant. In such cases, complete control of the reaction is hardly possible. Similar conditions exist also during block copolymer formation by melt coupling reactions. To overcome this problem we introduced a new type of coupling agent which contains two different reactive groups [20–22]. The structure of the coupling agent is shown below.

The coupling agent possesses one oxazoline group that reacts preferably with carboxylic groups and one oxazinone group that reacts with amino or hydroxy groups. The reactions are highly selective and were utilized in chain extension of AB polyamides [21] and synthesis of polyether–polyamide block copolymers [22].

This publication concerns the preparation of segmented block copolymers based on carboxy terminated PBT and amino group terminated PA12 by using the bifunctional coupling agent shown below. For comparison purposes, the possibility to obtain block copolymers by trans-reactions and condensation reactions of the terminal groups was also considered.



2. Experimental

2.1. Materials

Hydroxy terminated PBT with a molar mass of 2900 g/mol ($[\text{COOH}] = 68 \text{ mmol/kg}$, $[\text{COOCH}_3] = 79 \text{ mmol/kg}$, $[\text{OH}] = 975 \text{ mmol/kg}$, $T_m = 213 \text{ }^\circ\text{C}$) and two samples of amino group terminated PA12 with molar masses of 2000 g/mol ($[\text{COOH}] = 7 \text{ mmol/kg}$, $[\text{NH}_2] = 1000 \text{ mmol/kg}$, $T_g = 31 \text{ }^\circ\text{C}$, $T_m = 166 \text{ }^\circ\text{C}$) and 5000 g/mol ($[\text{COOH}] = 7 \text{ mmol/kg}$, $[\text{NH}_2] = 476 \text{ mmol/kg}$, $T_g = 39 \text{ }^\circ\text{C}$, $T_m = 174 \text{ }^\circ\text{C}$), respectively, were supplied by Degussa AG (Germany). The molar masses of the PA12 samples were controlled by 4,4'-diaminodicyclohexylmethane. Other solvents and chemicals are purchased from Merck and used without further purification.

2.2. Bifunctional coupling agent

The bifunctional coupling agent was prepared as described elsewhere [20].

2.3. Carboxy group terminated PBT

Carboxy group terminated PBT was obtained by reaction of hydroxy terminated PBT with succinic anhydride in the Haake extruder Rheomex PTW 16/25 (co-rotating twin screw extruder, screw diameter = 16 mm, $L/D = 25$, 100 rpm) at 250 °C. To remove small residues of unconverted succinic

Table 1
Sample overview

Sample ^a	Mixing time ^b (min)	η_{inh}^c (dL/g)
PBT-OH	—	0.154
PBT-COOH	—	0.154
PA12-NH ₂ (2000)	—	0.280
PA12-NH ₂ (5000)	—	0.400
Block PA12/PBT (1a)	0	0.244
Block PA12/PBT (1b)	2.5	0.478
Block PA12/PBT (1c)	5.0	0.509
Block PA12/PBT (1d)	10.0	0.570
Block PA12/PBT (2a)	0	0.365
Block PA12/PBT (2b)	10.0	0.757

^a Block copolymers **1a–d** and **2a,b** were prepared using PA12-NH₂ (2000) and PA12-NH₂ (5000), respectively.

^b DACA Micro-Compounder, 230 °C, 100 rpm.

^c Measured in *m*-cresol, 25 °C, $c = 0.5 \text{ g/dL}$.

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