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The effect of additives and complexing agents on the synthesis and thermo-oxidation stability of poly(butylene terephthalate)

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ABSTRACT

In this paper we report a comparative study about the effect of several additives and complexing agents on the synthesis and stability of poly(butylene terephthalate) (PBT) synthesized in the presence of the standard catalyst $Ti(O-nBu)_4$. Among the used additives, very surprisingly acetylacetone showed a deep influence on the catalysis and the properties of the final PBT. In particular the polymer was obtained in a shorter reaction time and with higher thermo-oxidation stability. On the contrary the simple $Ti(O-nBu)_4$, the well-known standard catalyst, resulted the more deleterious for the properties of the polymer. Moreover, for a useful comparison, a stabilized PBT was synthesized in the presence of $Ti(O-nBu)_4$ with the addition of the stabilizer U626.

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KEYWORDS

PBT;
Titanium;
Catalysis;
Stabilization;
Additives.

INTRODUCTION

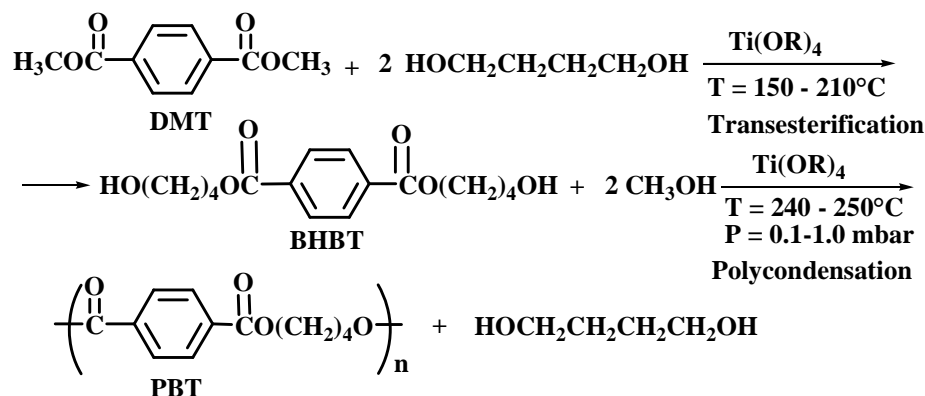
Poly(butylene terephthalate) (PBT) is one of the most important thermoplastic polyesters and is largely used to produce fibers as well as in motor and electric industry^[1-4]. PBT synthesis is generally performed in two steps: the transesterification of dimethyl terephthalate with 1,4-butanediol, and the following polycondensation of the resulting oligomers under dynamic vacuum (SCHEME 1). Both the steps are catalyzed by Ti(IV) alcolates that can be used for industrial and laboratory scale.

Important aims of the current research concern the

development of more active catalytic systems and the improvement of the properties of the final polymer. Both the aspects are very important from an economical, scientific and industrial point of view.

On one hand poly(ethylene terephthalate) (PET) has been much more studied and several efficient catalytic systems have been developed^[4-8]; in this case, in order to suppress undesired side reactions, phosphorous-based compounds (phosphate salts, alkyl phosphates, alkyl phosphonates) are added to stabilize both transesterification and polycondensation catalyst^[4,9-11].

On the other hand PBT has received much less attention and only few alternatives to the standard Ti(IV)



SCHEME 1

alcolates catalysts are available^[12-15]. Very interestingly Colonna et al. reported that the addition of a phosphate as co-catalyst to the titanium alcolates and hafnium catalysts led to a higher polymerization rate in PBT synthesis^[13]. Moreover, the use of phosphates improved the thermal stability of the final polymers^[13].

The study of degradation and stabilization of polymers has a great impact especially on the final applications and the life of the materials. Several studies on the thermal and thermo-oxidative degradation of polyesters showed that PBT is less stable than PET. For this reason stabilization, using a radical scavenger, is usually required for long life PBT based materials^[16-19]. In general the thermo-oxidation of organic compounds and polymers is a radical chain process. On the basis of the reported thermo-oxidation degradation mechanisms^[16-19], the residual of the catalyst can have an important influence on the stability of polyesters. For these reasons in the past years, apart from the use of commercially available stabilizers, we considered different approaches for the stabilization of polyesters. We focused our attention on the possibility to increase the stability of PBT polymers with the modification of the catalyst composition^[12].

On the basis of these considerations in this article we report the results on the effect of several additives/complexing agents both on the catalysis and on thermo-oxidation stability of PBT. The attention was addressed to two types of compounds: complexing agents with the ability to chelate metal cations and phosphonate type compounds, well-known additives for the stabilization of PET catalysts^[9-11].

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT) was supplied and used without further purification from NGP S.p.A.; 1,4-butanediol (1,4-BD) from BP; Ti(O-nBu)_4 , acetylacetone, ethylacetoacetate, Na_2EDTA , triethyl phosphoneacetate and triethylphosphoneformiate were purchased from Aldrich; the stabilizer U626 was purchased from general electric.

Instrumental and analysis

Large scale polymerisation was performed in a 20 L steel reactor heated with electric resistance and equipped with mechanical stirrer (driven at variable rpm), a strain-gauge sensor mounted on the stirrer shaft in order to monitor the melt viscosity (and indirectly the increase of molecular weight) during the polymerisation, a distillation column with a water condenser, a vacuum oil pump (mod. Edwards E2M-12) with a liquid nitrogen trap. The reaction temperature was increased at a fixed heating rate according to standard procedures. All of the processing parameters were monitored by electronic recorders.

Thermal measurements were performed by a DSC-7 Perkin-Elmer calorimeter under nitrogen flow, at $10^\circ\text{C}/\text{min}$ rate for both heating and cooling. The symbols T_m , ΔH_m , T_{mc} , ΔH_{mc} , respectively refer to melting temperature, melting enthalpy, temperature of crystallization from melt, enthalpy of crystallization from melt.

The intrinsic viscosity (I.V.) was determined measuring the dropping time at 30°C in an auto viscosim-

eter Shotte-Gerate of solution of 0.600 g of PBT in 50.0 ml of *o*-chlorophenol. The I.V.s were determined with an accuracy of ± 0.002 (dL/g).

Wide-angle X-ray diffraction patterns, with nickel filtered Cu K α radiation, were obtained, in reflection, with an automatic Bruker D8 Advance diffractometer. The spectra were detected on 30 μ m film.

Color L and color b, according to Cielab scale, were determined on the pellets using a colorimeter BYK Gardner.

Accelerating thermo-oxidation tests were performed in a forced circulating air oven model WTC BINDER FD53 at 160°C. In the oven 5 identical samples of 100g of pellets (pellet dimensions: 3 \times 3 \times 2mm) of PBT were put in bakers of perfectly identical shape. Every sample was taken out of the oven at different times, and color and I.V. were measured according to the above procedures.

Typical experimental procedure for the synthesis of the catalytic systems

In an oven-dried two-necked round-bottom flask, a solution of Ti(O-*n*Bu) $_4$ (20.2mmol), in dry 1,4-butanediol (50mL) was heated under nitrogen at 100°C, for 1h. Then the additive (40.4mmol) was added and the solution was stirred at 80°C for 1h. The obtained solution was used in the synthesis of PBT without any other treatment.

Pilot plant polymer synthesis

In a typical synthesis

8000g (43.50 mol) of DMT and 4825g (53.61mol) of 1,4-BD were introduced into the reactor. The mixture was heated at 145°C under stirring at atmospheric pressure and, at this temperature, the solution of 20.2mmol of the titanium(IV) alcolate and 40.4 mmol of the additive in 1,4-butanediol were added to the melt. Then the temperature was raised to 230°C. During this period, transesterification proceeded till the complete distillation of methanol. Then the pressure was reduced in the range 0.5-1.0 mbar and the temperature increased to 255°C. These are the conditions for the polycondensation stage, in which the molecular weight increases and 1,4-BD was distilled off. The synthesis was monitored with an electronic torque-meter and the reaction was stopped at an I.V. in the range of 0.83-0.89dL/g.

Then the reactor was pressurized at 1.1 bar with nitrogen and the polymer was extruded and granulated. In the synthesis of stabilized PBT 7, the stabilizer U626 was added to the reaction mixture at the end of the transesterification stage as a mixture of 8g in 80g of 1,4-BD.

RESULTS AND DISCUSSION

Library of Ti(IV) catalysts: evaluation of several additives/complexing agents

The first aim of this study was the elaboration of a reliable method to test the effectiveness of several additives in PBT synthesis. In the selection of the additives, we took into account well-known metal complexing agents or compounds that are usually used as metal stabilizers in polyester synthesis^[9-11]. Every compound was introduced in PBT synthesis as solution in 1,4-BD together with Ti(IV) alcolate; the additive/Ti(IV) molar ratio was 2(for the preparation of the catalytic solutions see experimental part). The used additives are described in figure 1.

It is important to note that commercially available complexes are reported of both acetylacetone and ethylacetoacetate^[12,20]; EDTA is a well-known chelating agent. A different approach was considered for the choice of TEPF and TEPA. TEPA as a phosphonate type compound, is used as stabilizer for transesterification catalysts in PET synthesis^[9-11]. It is used to avoid

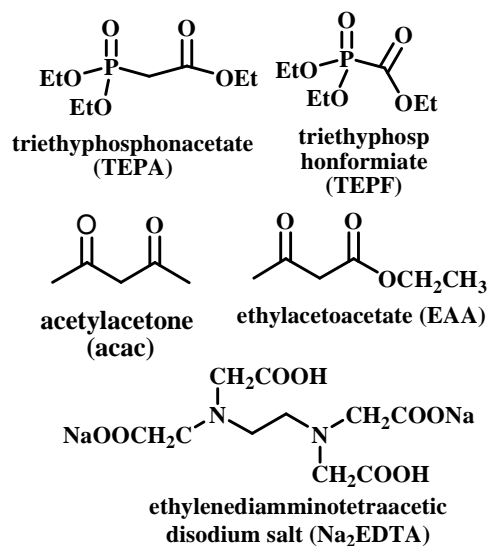


Figure 1

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undesired side reactions that affect the properties of the obtained PET^[9-11]. With the use of TEPA and TEPF we wanted to test if these compounds have the same effect on the stability of PBT polymers.

New Ti(IV) catalytic systems in the synthesis of PBT

After the selection of the additives and the preparation of the catalytic solutions in 1,4-butanediol, the efforts were devoted to determine their effectiveness in large scale synthesis of representative PBTs in the same reaction conditions. Furthermore a stabilized PBT (entry 7) was synthesized in the presence of Ti(O-nBu)₄ as catalyst with the addition of the stabilizer U626 (Ultranox 626): in this case the aim was to compare the properties of stabilized and not stabilized PBTs. The characteristics of the synthesized polymers are summarized in TABLE 1.

Even if from the analysis of the obtained data, all the catalysts showed acceptable activity and yielded the polymers in reasonable reaction time with good intrinsic viscosity (I.V.), significant differences can be noted. In particular, the acetylacetonate-titanium(IV) system (entry 2) showed higher activity than all the Ti(IV) based catalytic systems for both transesterification (EI) and polycondensation (PC) stages. In fact, PBT 2 was obtained in a shorter reaction time and, according to the determined intrinsic viscosities, with high molecular weight. Only in entry 5, in the presence of Ti(IV)/TEPF system, we report a polymer with higher I.V. even if the reaction time was longer.

To confirm the validity of the experiments, the synthesis of the representative polymers (entries 1–7) were repeated in the same reaction conditions. In all the cases, the results were comparable to those reported in TABLE 1.

In general the color and the appearance of polymers has a great importance from economical and practical point of view. The color of polymers can be numerically measured in terms of L-value and b-value directly on the pellets, according to Cielab scale (TABLE 1). L-value is related to the degree of whiteness with a greater numerical value showing a higher (desirable) whiteness. The whiteness and consequently color L is usually related to the level of crystallinity of polyesters. The b-value is related to the degree of yellowness, and

TABLE 1: characteristics of PBT synthesized in the presence of new catalytic systems

Entry	Catalyst	EI stage Time(min.)	PC Stage Time(min.)	I.V. (dL/g)	Color L	Color b
1	Ti(O-nBu) ₄	86	87	0.855	89.9	2.77
2 ^a	Ti(O-nBu) ₄ + acetylacetonone	67	83	0.851	79.5	3.20
3 ^a	Ti(O-nBu) ₄ + EDTA	75	90	0.843	88.9	3.90
4 ^a	Ti(O-nBu) ₄ + EAA	84	91	0.828	89.8	1.82
5 ^a	Ti(O-nBu) ₄ + TEPF	85	91	0.875	89.0	4.11
6 ^a	Ti(O-nBu) ₄ + TEPA	81	89	0.849	89.2	4.02
7 ^b	Ti(O-nBu) ₄ + U626	85	85	0.829	90.6	5.51

^aThe catalytic system was prepared according to the procedure reported in the experimental section; ^bThe stabilizer U626 was added in the course of the synthesis.

TABLE 2: Thermal analysis of PBT 1 and PBT 2

Sample	Catalyst	T _m ^(a)	$\frac{\Delta H_m}{J g^{-1}}$ ^(b)	T _{m c} ^(c)	$\frac{\Delta H_{mc}}{J g^{-1}}$ ^(d)
1	Ti(O-nBu) ₄	223	47.5	178	-48.2
2	Ti(O-nBu) ₄ + acetylacetonone	219	45.2	175	-41.3

^aT_m refers to melting temperature; ^b ΔH_m is the melting enthalpy; ^cT_{m c} refers to the temperature of crystallization from melt; ^d ΔH_{mc} is the enthalpy of crystallization from melt.

a higher numerical value shows a higher (undesirable) degree of yellowness. A particular importance is attributed to the significance of color b: this parameter is usually related to the level of degradation of macromolecules. In fact many studies demonstrate that degradation processes usually led to conjugated or oxidized moieties that absorbs in near UV^[21].

In our work, all the samples can be considered very similar in terms of color b (the degree of yellowness), but surprisingly color L (the level of whiteness) is significantly lower for the polymers synthesized in the presence of titanium(IV)-acetylacetonate catalytic systems (PBT 2). This phenomenon can be related to a lower level of crystallinity and a poor tendency to crystallize, as confirmed by lower values of T_m, ΔH_m , T_{m c} and ΔH_{mc} of PBT 2 with respect to PBT 1 of the reported thermal analysis (TABLE 2). On the contrary, X-ray diffraction spectra on 30 μ m films (figure 2) have not shown particular differences between the two polymers.

Thermo-oxidation stability of the synthesized PBT

The evaluation of the stability to the thermo-oxidation of the PBTs was carried out by means of the age-

ing of great amount of pellets in forced circulating air oven: this is considered the more reliable method in order to test the stability to the thermo-oxidation^[18,22]. In practice, we put a series of five identical samples for each polymer in the oven at 160°C and we measured, at different times, color-L (TABLE 3), color-b (TABLE 4), intrinsic viscosity (I.V.; TABLE 5) for the treated samples.

In the comparison of the reported data, PBT 2, synthesized with Ti(IV)/acetylacetonate system, shows higher thermo-oxidation stability. It is worthy to note that PBT 2 suffers a very slight discoloring with a constant degree of whiteness (Color-L, TABLE 3), a very reduced increase of yellowness (color-b, TABLE 4) and surprisingly a slight increase of I.V. (see TABLE 5).

The trend of I.V. in PBT 2, since it cannot be related to the accuracy of the method (0.002 dL/g, see experimental section), is very interesting. If on one hand the slight decrease from 7 to 47h can be easily attributed to a slight degradation, the increase after the first 7h can be related to a very small increase of molecular weight. Usually SSP (solid state polycondensation) requires different reaction conditions^[23-26] but the possibility of milder conditions for SSP is very intriguing. This aspect is still under investigation.

The behavior of Color L in PBT 2 is very peculiar and has to be noted (TABLE 3). The significant improvement of color L (and of the related level of whiteness), after the first 7 hours of heating, can be related to the annealing that crystallizes the otherwise crystallinity-retarded polymer.

The use of the stabilizer U626 has a positive effect on the stability of the polymer obtained in the presence of Ti(O-nBu)₄; in fact in PBT 7 both the discoloring and the decrease of the intrinsic viscosity (I.V.) are smaller than those observed in PBT 1.

All the other catalytic systems influence negatively the properties of the polymers, but the behavior of the Ti(IV)/ethylacetoacetate system is less deleterious on thermo-oxidation stability. Very interestingly in this case we can note for color L, I.V. and color b a trend similar to that shown by stabilized PBT 7.

In conclusion, the relationship between the catalyst composition and the stability of the obtained polymer is very peculiar. On one hand the simple Ti(O-nBu)₄ is more deleterious, on the other it is very interesting to

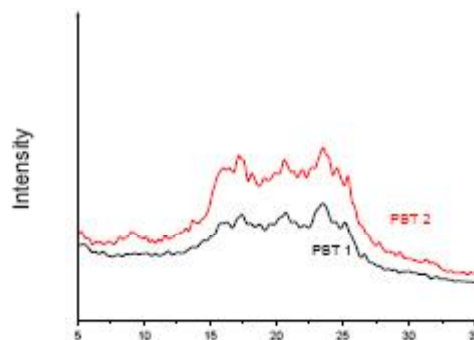


Figure 2: X-ray diffraction spectra of PBT 1 and PBT 2

TABLE 3: Color-L of the PBT polymers after the oven ageing at 160°C at different time

Entry	Catalytic systems	Color L at different ageing Time (h)				
		0	7	23	31	47
1	Ti(O-nBu) ₄	89.9	88.4	85.2	85.4	83.6
2	Ti(O-nBu) ₄ +acetylacetonate	79.5	86.7	86.3	86.1	86.0
3	Ti(O-nBu) ₄ + EDTA	88.9	88.0	86.6	85.5	84.8
4	Ti(O-nBu) ₄ + EAA	89.8	89.9	89.6	89.1	88.1
5	Ti(O-nBu) ₄ + TEPF	89.0	87.8	85.3	86.7	84.0
6	Ti(O-nBu) ₄ + TEPA	89.2	88.2	87.3	86.4	84.3
7	Ti(O-nBu) ₄ + U626	90.6	89.4	86.7	86.2	84.9

^aT_m refers to melting temperature; ^bΔH_m is the melting enthalpy; ^cT_{mc} refers to the temperature of crystallization from melt; ^dΔH_{mc} is the enthalpy of crystallization from melt.

TABLE 4: Color-b of the PBT polymers after the oven ageing at 160°C at different time

Entry	Catalytic systems	Color b at different ageing time (h)				
		0	7	23	31	47
1	Ti(O-nBu) ₄	2.77	12.50	17.9	19.8	21.9
2	Ti(O-nBu) ₄ +acetylacetonate	3.20	5.00	5.90	6.69	7.47
3	Ti(O-nBu) ₄ + EDTA	3.90	5.90	11.12	15.31	17.90
4	Ti(O-nBu) ₄ + EAA	1.82	6.67	11.48	12.81	14.66
5	Ti(O-nBu) ₄ + TEPF	4.11	13.46	17.60	18.00	19.50
6	Ti(O-nBu) ₄ + TEPA	4.02	12.40	15.55	17.34	18.72
7	Ti(O-nBu) ₄ + U626	5.51	8.80	12.70	13.41	14.63

TABLE 5: I.V. of the PBT polymers after the oven ageing at 160°C at different time

Entry	Catalytic systems	I.V. (dL/g) at different ageing time (h)		
		0	7	47
1	Ti(O-nBu) ₄	0.855	0.827	0.753
2	Ti(O-nBu) ₄ +acetylacetonate	0.851	0.860	0.855
3	Ti(O-nBu) ₄ + Na ₂ EDTA	0.843	0.823	0.768
4	Ti(O-nBu) ₄ + EAA	0.828	0.819	0.783
5	Ti(O-nBu) ₄ + TEPF	0.875	0.852	0.785
6	Ti(O-nBu) ₄ + TEPA	0.849	0.821	0.777
7	Ti(O-nBu) ₄ + U626	0.829	0.806	0.790

note that the level of influence on the catalysis and the properties of the polymer depends on the type of the additive. The greater stability of PBT 2 can be prob-

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ably attributed to the deactivation of Ti(IV) due to the complexation of the acetyl acetone that suppresses the degradation reactions. The development of a reasonable model of the degradation pathway is under investigation and will be the subject of the next paper.

CONCLUSIONS

In this paper we report a comparative study about the influence of several additives on the synthesis and stability of poly(butylene terephthalate) (PBT) synthesized in the presence of the standard catalyst $\text{Ti}(\text{O-nBu})_4$. Among the tested additives, very surprisingly acetylacetone showed a deep influence on the catalysis and the properties of the PBT. In particular the polymer was obtained in a shorter reaction time and with a higher thermo-oxidation stability with respect to the standard PBT without any additive. Both these results are very important from scientific and economical point of view. In fact a more active catalytic system means a reduction of the cost of production of the polymer; while higher thermo-oxidation stability improves the durability of the manufactures and allows to avoid the use of stabilizers. On the basis of this work, further studies are in course to evaluate the effectiveness of other additives on the catalysis and the stability of PBT polymers. We are also investigating about the hypothesis of a reasonable mechanism on the relationship between the catalyst composition and PBT properties.

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