**Sławomir Dutkiewicz,
Jacek Wesołowski,
Dawid Chojnacki,
Danuta Ciechańska**

Institute of Biopolymers and Chemical Fibres,
ul. M. Skłodowskiej-Curie 19/27 Łódź, Poland
E-mail: grupasyntez@ibwch.lodz.pl

Method to Produce Biodegradable Aliphatic-Aromatic Co-Polyesters with Improved Colour

Abstract
A family of biodegradable aliphatic-aromatic co-polyesters (BAAC) was prepared by polycondensation in the melt. The synthesis was carried out with the addition of a small amount of alkaline metals salts which produced the effect of a distinctly improved colour of the polyesters as registered in the L, a*, b* system. The yellow index of the tested samples was calculated from the chromaticity coordinates X, Y, Z. The colour could have been further improved by an exposure to UV radiation. No change was observed in the average molecular mass of the tested co-polyesters as result of the exposure, while an insignificant drop occurred of the inherent viscosity.*

Key words: *biodegradable aliphatic-aromatic co-polyesters, colour parameters, yellowness index.*

Introduction

Industrial and municipal wastes are an ever increasing problem and menace to the environment. One of the waste components is durable synthetic resins which degrade very slowly. Recycling and incineration used so far are not the best way to solve the problem. New ways are to be sought to produce alternative materials that can be biologically recycled, and which would be prone to degradation with the delivery of harmless substances as post-use materials. Resins based on biodegradable polymers belong to materials which can be divided into two groups: crude oil-based polymers and those derived from natural resources. Both material groups arouse an ever-increasing interest in many application domains, and their production is on the rise.

Aliphatic-aromatic co-polyesters are compounds known since quite a long time; the polymers, however, with their physical-mechanical features could not face competition with commercial commodity polyesters like poly(ethyleneterephtalate) or poly(butyleneterephtalate). It was only the discovery of the resins' biodegradability that opened new directions. The mid-90s saw a lot of studies related to earlier works in the synthesis and properties of biodegradable aliphatic-aromatic co-polyesters. The new studies explained the relationship between structure, physical-chemical properties and biodegradability of the polymers [1 - 5]. Although not derived from renewable resources, the polymers and post-use materials are prone to complete biodegradation, thus posing no threat to the environment [6]. Very recent investigations have also shown that the kind of co-polyester can be prepared in a substantial part from renewable materials [7, 8]. Poly(butylene adipate-co-terephthalate) made by BASF under the trade name Ecoflex is a commercially available material of this kind. Actually, the biodegradable aliphatic-aromatic co-polyesters appeared to be an alternative in some application domains of the biodegradable polymers.

Commercial resins have to respond to a number of quality demands. Colour is one of the critical parameters whenever the aesthetics of the final product are considered.

Figure 1. *Hue of co-polyester granulate made without the modifying additive.*

Figure 2. *Hue of co-polyester granulate made with a modifying additive.*

Technology outlines have been prepared in the Institute of Biopolymers and Chemical Fibres (IBWCh) for the production of poly(butylene succinate-co-glutarate-co-adipate-co-terephthalate (BAAC) synthesised by melt polycondensation. The co-polyester revealed very good biodegradability and physical-chemical properties adequate for processing. As demonstrated in application trials, melt-blown and spunbonded non-wovens could have been made from it. Both the granulate and the products made from it had a rose hue. The feature is inacceptable in the processing of textiles (***Figure 1***).

It was an aim of our work to improve the colour of the biodegradable co-polyester. This could have been attained by adding environmentally-friendly inorganic modifying agents to the co-polyester in the phase of its synthesis (***Figure 2***)

A further improvement of the colour resulted from the exposure of the co-polymer granulate to UV radiation. Basic colour parameters and a decrease of the yellowness index were estimated. It was documented that 60-hours exposure to UV radiation at the applied wavelength did not affect the average molecular mass of the co-polyester.

Materials

- 1,4 – Butanediol ≥ 99.5% Sigma-Aldrich (USA)
- Dimethylterephtalate (DMT) Mogilewo Belorus
- Titanium(IV)butoxide 97% Sigma-Aldrich
- Dimethylsuccinate 99% Merck (USA)
- Dimethylglutarate 98% Alfa Aesar (USA)

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- Dimethyladipate 99% Merck
- Uniestrol - content of esters 99% - a blend of dimethyl esters of aliphatic dicarboxylic acids composed of:
  - Dimethylsuccinate 13%
  - Dimethylglutarate 53.8%
  - Dimethyladipate 33.2%

Made by „Organika" Ltd. Nowa Sarzyna, Poland

- Sodium bicarbonate ≥ 99.5% Sigma-Aldrich
- Sodium carbonate ≥ 99.0% Sigma-Aldrich
- Potassium bicarbonate ≥ 99.7% Sigma-Aldrich
- Potassium carbonate ≥ 99.0% Sigma-Aldrich
- Lithium carbonate ≥ 99.0% Sigma-Aldrich
- Chloroform 99.0% POCh (Polish producer of reagents).

All of the used materials were of high purity and did not contain impurities that could affect the colour of the prepared co-polyesters. The material properties were tested in an accredited analytical laboratory of IBWCh and the Polish Academy of Sciences, Department Łódź

Synthesis of the co-polyesters

Synthesis of poly(butylene succinate-co-terephthalate) - BAAC

A 0.9 dm^3, stainless steel reactor equipped with an agitator was used in the synthesis. It was filled with: 97 g of dimethylterephtalate (DMT), 109.5 g of dimethylsuccinate, 150 g of butanediol and 0.05 g of titanium(IV)butoxide catalyst. The mixture was heated to 160 °C under nitrogen and the ester exchange was made at a temperature rising from 60 to 220 °C with the delivery of methanol. Then, a second portion of the titanium(IV)butoxide catalyst in the amount of 0.15 g was added to the reacting mass. The pressure was step-wise reduced and an excess of 1,4-butanediol was distilled. The polycondensation reaction proceeded at 250 °C and pressure of 0.54 hPa. The obtained co-polyester was pressed out of the reactor after 80 minutes in the form of a strand which was cut into granulate.

Synthesis of poly(butylene glutarate-co-terephthalate)

A 0.9 dm^3, stainless steel reactor equipped with an agitator was used in the synthesis. It was filled with 97 g of dimethylterephtalate, 120 g of dimethylglutarate, 150 g of butanediol and 0.05 g of titanium(IV)butoxide catalyst. The mixture was heated up to 160 °C under nitrogen. Ester exchange and polycondensation reactions were carried out as for BAAC.

Synthesis of poly(butylene adipate-co-terephthalate)

A 0.9 dm^3, stain-less steel reactor equipped with an agitator was used in the synthesis. It was filled with 97 g of dimethylterephtalate, 130.5 g of dimethyladipate, 150 g of butanediol and 0.05 g of titanium(IV)butoxide catalyst. The mixture was heated up to 160 °C under nitrogen. Ester exchange and polycondensation reactions were carried out as for BAAC.

Synthesis of poly(butylene succinate-co-glutarate-co-adipate-co-terephthalate)

A 0.9 dm^3, stain-less steel reactor equipped with an agitator was used in the synthesis. It was filled with 97 g of dimethylterephtalate, 120 g of Uniestrol preparation, 150 g of butanediol, 0.05 g of titanium(IV)butoxide catalyst, and 0 to 0.228% of an adequate carbonate or bicarbonate, screened through a 50 μm mesh. The mixture was heated up to 160 °C under nitrogen. Ester exchange and polycondensation reactions were carried out as for BAAC.

All of the co-polyesters were prepared with a 60/40 proportion of the acidic aliphatic to aromatic components at the start of the synthesis. All syntheses had a smooth, undisturbed run.

Characteristic of the molecular masses by gel chromatography

The following outlines the parameters of the chromatography analysis:

- Solvent (moving phase): chloroform
- Column: Plgel Mixed C, 300 mm, 5 μm (Polymer Laboratories Ltd.)
- Temperature of column: 35 °C,
- Stream rate: 0.7 ml/min,
- Injection volume: 100 μl,
- Calibration standards: polystyrene with molecular mass from 580 to 3,993,000 and polydispersity from 1.04 to 1.14 (Polymer Laboratories).

Measurements of the co-polyester colour

The hue of the aliphatic-aromatic co-polyesters was measured in the systems L*, a*, b*, [9, 10] and X, Y, Z where:

X, Y, Z – chromaticity coordinates

L* - total light reflected by the sample of the aliphatic-aromatic co-polyester.

a* (+,–) – factor indicating the degree of change from green hue (negative values) to red hue (positive values).

b* (+,–) – factor indicating the degree of change from blue hue (negative values) do yellow hue (positive values).

The given values of the colour parameters are an average of five consecutive single measurements.

Colourimeter: „Colour and colour digital differential meter" model ND-101 D Nippon Denshoku Kogyo co., Ltd, Japan.

Yellowness index of the co-polyester samples was calculated from the equation:

$$IY = 100\,(CxX - CzZ)/Y \qquad (1)$$

where:

$C_X = 1.28$ and $C_Z = 1.06$ factors for ***Equation 1*** [10].

Estimation of inherent viscosity

The outflow time of the solutions of the co-polyesters in chloroform was measured with an Ubbelode viscometer with capillary 0A and the constant K = 0.00498 at temperature of 25 °C. The value of inherent viscosity was calculated from the equation:

$$\eta_{inh} = (\ln (t_r/t_o))/c$$

t_r - outflow time of the co-polyester solution,

t_o - outflow time of the solvent,

c - concentration of the co-polyester in the solution - 0.2 g/dl.

UV irradiation of the co-polyesters

Two lamps, 6 W each, emitting UV 386 nm waves were used to this end.

Discussion of obtained results

It was found in the research concerned with BAAC that the dimethyl ester of adipic acid used in the raw materials composition was responsible for the rose

Table 1. *Results of colour measurements of BAAC obtained with the participation of one aliphatic acidic component.*

No.	Composition of the co-polyester	L*	a*	b*
1.	poly(butylene terephthalate-co-succinate	80.7	-2.7	4.7
2.	poly(butylene terephthalate-co-glutarate	82.1	-3.8	3.1
3.	poly(butylene terephthalate-co-adipate	61.2	21.1	14.2

Table 2. *Colour measurement of poly(butylene succinate-co-glutarate-co-adipate-co-terephthalate)'s BAAC made with and without inorganic modifying additives*

No.	Modifying additive	L*	a*	b*
1.	-	47.7	24.1	18.1
2.	0.176% Na_2CO_3	75.5	-0.8	15.1
3.	0.215% Na_2CO_3	68.0	6.2	17.9
4.	0.280% $NaHCO_3$	68.7	2.9	17.5
5.	0.228% K_2CO_3	77.1	-2.5	12.5
6.	0.228% $KHCO_3$	75.1	-2.1	12.5
7.	0.124% Li_2CO_3	66.9	8.0	20.9

Table 3. *Colour measurements of BAAC poly(butylene succinate-co-glutarate-co-adipate-co-terephthalate) after exposure to UV radiation.*

No.	Modifying additive	Time of exposure to UV, h	L*	a*	b*
1.	Without additive	0	47.7	24.1	18.1
		24	56.5	17.7	15.9
		30	59.4	15.4	15.9
		60	62.7	11.3	16.6
2.	0.176% Na_2CO_3	0	75.5	-0.8	15.1
		24	78.2	-3.4	9.3
		40	78.5	-3.4	7.4
		60	78.9	-3.5	7.0
3.	0.215% Na_2CO_3	0	68.0	6.2	17.9
		20	74.,5	0.0	15.3
		40	77.3	-2.7	13.0
		60	79.7	-4.0	8.0
4.	0.280% $NaHCO_3$	0	68.7	2.9	17.5
		18	74.4	-2.4	12.4
		24	74.6	-2.7	11.8
		60.	77.1	-3.3	10.1
5.	0.228% K_2CO_3	0	77.1	-2.5	12.5
		20	78.1	-3.4	8.6
		30	78.7	-3.5	7.7
		60	78.7	-3.3	7.1
6.	0.228% $KHCO_3$	0	75.1	-2.1	12.5
		20	77.6	-3.6	8.7
		30	77.8	-3.7	7.7
		60	77.9	-3.3	6.8
7.	0.124% Li_2CO_3	0	66.9	8.0	20.9
		24	76.1	-1.7	14.2
		40	77.5	-3.3	12.0
		60	78.7	-3.7	10.7

colour appearing in the co-polyesters. The conclusion was made on the basis of an experiment in which three different co-polyesters were prepared with three different acidic aliphatic components: poly(butylene succinate-co-terephthalate), poly(butylene glutarate-co-terephthalate) and poly(butylene adipate-co-terephthalate), using the three different dimethyl esters, succinate, glutarate and the afore-mentioned adipate, in their synthesis. Colour measurements for the materials were made in the L*, a* ,b* system.

From the colour measurements, it appears that the co-polyester made with the participation of the dimethyl ester of adipic acid displays a low brightness parameter (L*) and high values of the colour coordinates a* and b*, witnessing a high share of red and yellow colour in the tested sample (see ***Table 1***). The co-polyester poly(butylene succinate-co-glutarate-co-adipate-co-terephthalate), which is the subject of the herein described investigation, exhibits a similar colour characteristic. It was made with the use of the Uniestrol (trade name) preparation, a blend of all three earlier mentioned esters: dimethyl succinate, dimethyl glutarate and dimethyl adipate, which bestows the rose colour on the final product.

The influence of the dimethyl ester of adipic acid on the appearance of the rose colour is also confirmed with investigations made by other research centres in the application of the material [11].

In the course of our investigation, in the modification of crystallising properties of co-polyesters by nucleation, we discovered an improvement in the colour of the obtained poly(butylene succinate-co-glutarate-co-adipate-co-terephthalates) BAAC. The effect was produced by the addition of modifying agents – bicarbonates or carbonates of alkaline metals to the reaction mixtures. Sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate and lithium carbonate were used as modifying additives. Colour was estimated in the obtained co-polymers.

Colour parameters were improved for the BAACs prepared with modifying additives. The brightness index L* increased remarkably, while the colour coordinate a* was decreased, witnessing the favourable decrease of the red component. 0.176% of sodium carbonate, 0.228% of potassium carbonate and 0.228% of potassium bicarbonate appeared to be the most effective modifiers. The colour parameter b*, which shows the yellow component, was barely changed for all modified BAACs. The use of the additives had a distinct effect upon the visual appearance of the granulate. The granulate without additives had a rose hue (***Figure 1***), while the others prepared with modifying agents (***Table 2***) were of a light-creamy colour (***Figure 2***).

The herein related data concerning the modification of poly(butylene succinate-co-glutarate-co-adipate-co-terephthalate) BAAC are based on experiments only; we do not know the mechanism by which

the colour improvement of the investigated co-polyesters occurs.

The improvement of the colour was also achieved by exposure of the poly(butylene succinate-co-glutarate-co-adipate-co-terephthalate) BAAC granulates to UV radiation. For the UV-irradiated co-polymers, measurements of the colour parameters were made (***Table 3***).

In all of the BAACs prepared with and without modifiers, a further increase of the brightness parameter L* can be observed. The colour coordinate a* was decreased. The share of the red colour component is increased in the co-polyester without additives, while, in the modified polyesters, the parameter shifts toward small negative values which features the green colour. Coordinate b* is decreased in all of the co-polyesters, witnessing a decrease of the share of yellow colour. It can, moreover, be seen that after a 60 hours of UV irradiation, the final colour parameters for all of the modified BAACs are close to each other, regardless the value of the initial L*, a* and b* parameters. The test results of the colour change in the lithium carbonate-modified co-polyester are interesting in that the smallest amount of the modifying agent was used in its synthesis. Hence, the attained initial colour characteristic is the worst in that case. However, this improves after 60 hours of UV irradiation, matching the values of the other BAACs. The positive change of the colour parameters is confirmed as well, with the decrease of the yellowness indices determined on the basis of the measured chromaticity coordinates X, Y, Z. The indices decrease with prolonged UV irradiation time, which is illustrated with ***Figure 3***.

The yellowness index values of co-polyesters prepared without colour-improving additives place themselves on a much higher level in comparison to the remaining polyesters.

It is noteworthy to observe that the drawn curves of the yellowness index decrease for BAACs, prepared with 0.228% of potassium carbonate and bicarbonate, coincide and attain the lowest values before and after irradiation.

The curve of yellowness index decrease for BAAC with 0.175% of sodium carbonate has a very similar shape.

To assess the stability of physical-chemical properties, the average molecular mass by GPC method and inherent viscosity of the BAACs were measured before and after the UV irradiation. The measurement results are compiled in ***Table 4***. It appears that after 60 hours of irradiation, the molecular mass values show no essential change, while some insignificant decreases occurred in the inherent viscosity value.

It is planned, in further investigations concerning the improvement of colour of BAAC poly(butylene succinate-co-glutarate-co-adipate-co-terephthalate), to employ other modifying additives and to optimise the content of the so far used modifiers in the reaction mix. UV irradiation with other wavelengths is also anticipated. It is intended to harness complementary analytical testing in the assessment of the stability of the physical-chemical properties.

Table 4. *Value of average molecular mass and inherent viscosity of BAAC before and after 60 hours of UV irradiation.*

Amount and kind of co-polyester colour-improving additive	Molecular mass before UV irradiation		η_{inh}, dl/g	Molecular mass after 60 hours UV irradiation		η_{inh}, dl/g
	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$		$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	
No additive	23.8	105.8	0.836	24.5	108.4	0.725
0.176% Na_2CO_3	21.3	78.8	0.690	21.7	78.5	0.655
0.215% Na_2CO_3	23.6	78.2	0.780	23.8	77.5	0.729
0.280% $NaHCO_3$	20.6	86.0	0.703	22.2	84.1	0.668
0.228% K_2CO_3	22.0	87.0	0.776	22.3	91.9	0.742
0.228% $KHCO_3$	22.0	89.4	0.703	22.9	90.4	0.720
0.124% Li_2CO_3	22.9	84.8	0.738	21.9	82.5	0.703

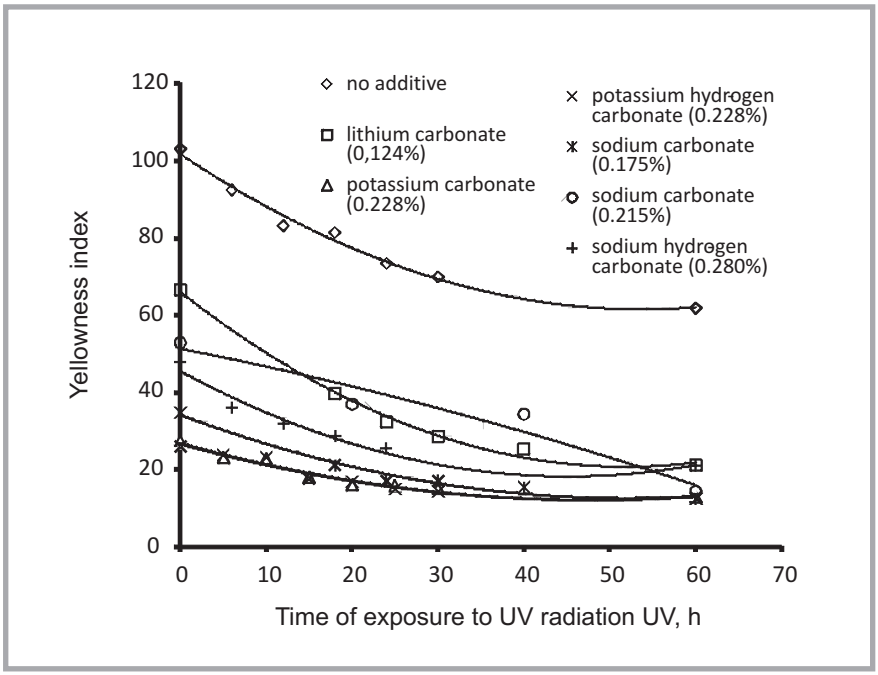

Figure 3. *Dependence of yellowness index on the time of exposure to UV radiation and the kind of modifying additive.*

Summary

- Biodegradable aliphatic-aromatic co-polyesters [poly(butylene adipate-co-glutarate-co-succinate-co-terephthalate)] were prepared by polycondensation in the melt. Co-polyesters made without a modifying additive were of a rose hue, which is an obstacle in the use of the material in many application domains. It was demonstrated that the co-polyesters are processable for manufacturing melt blown and spun-bonded non-wovens.
- Successful trials were made to improve the colour of BAAC by the addition of inorganic substances like carbonates or bicarbonates of alkaline metals in the phase of synthesis. The best colour improvement results were attained with the addition of 0.176% of sodium carbonate, 0.228% of po-

tassium carbonate or 0.228% of potassium bicarbonate.

- A further colour improvement in the prepared BAACs could have been achieved by the exposure of the granulates to UV radiation.
- The prepared method brings the chance of an evident improvement of the colour parameters L*, a*, b* and reduction of the material's yellowness expressed by yellowness index in the BAACs synthesised with dimethyl adipate as a component. The average molecular mass of the BAACs remains unchanged with the improvement of colour, while the inherent viscosity of the co-polyesters drops slightly.

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References

1. Witt W, Müller R, Deckwer W. New biodegradable polyester-copolymers from commodity chemicals with favorable use properties. *J. Environm. Polym. Degrad.* 1995; 3: 215.
2. Witt W, Müller R, Deckwer W. Biodegradation behaviour and material properties of aliphatic/aromatic polyesters of commercial importance. *J. Environm. Polym. Degrad.* 1997; 5: 81.
3. Witt W, Ening T, Yamamoto M, Kleeberg WD, Müller R, Deckwer W. Biodegradation of alphatic-aromatic copolyesters:evaluation oft he final biodegradability and ecotoxicological impact of degradation intermediates. *Chemosphere* 2001; 44: 289.
4. Mueller RJ. Biological degradation of synthetic polyesters-Enzymes as potential catalysts for polyester recycling. *Process Biochemistry*, 2006; 41: 2124.
5. Witt U, Mueller RJ, Deckwer WD. Biodegradation of polyester copolymers containing aromatic compounds. *Pure Appl. Chem.* 1995; 32: 851.
6. Gallagher FG, Hamilton CJ, Hansen SM, Tietz RF. *Polyester and their use in compostable products such as disposable diapers* US 5 171 308.
7. Koopman F, Wierckx N, Winde JH, Ruijssenaars HJ. Efficient whole-cell biotransformation of 5-(hydroxymethyl) furfural into FDCA, 2,5-furandicarboxylic acid. *Bioresource Technology*, 2010; 101: 6291.
8. Jiping M, Yi P, Min W, Jie X, Hong M, Xin N. The copolymerization reactivity of diols with 2,5-furanedicarboxylic acid for furan-based copolyester materials. *J. Mater. Chem*. 2012; 22: 3457.
9. Jaglarz J, Santera J, Cisowski J. Wrażenia barwne-jak je mierzyć? Foton 89, Lato 2005, p. 34.
10. Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Colour Coordinates for Yellowness Index per ASTM Method D 1925.
11. Cooke AW, Charlotte; Davies BL. Poly(butylenes terephthalate) copolyester and a process for preparing it. US 5 162 153.

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