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INFLUENCE OF FLAME RETARDANT AND PROCESSING CONDITIONS ON SELECTED PROPERTIES OF MOULDINGS MADE OF ABS

Thanks to dyeing of polymers, the possibilities of their use are constantly increasing. It is equally important to use additives that will have several functions. A perfect example is titanium dioxide used as an optical brightener and a flame retardant at the same time. Mostly it is used in the form of a powder. However, there are no studies where TiO_2 is used as a colourbatch based on the different polymer matrix.

The aim of the work was to investigate the effect of titanium white in the form of colourbatch on the flammability and selected properties of mouldings produced in various processing conditions. Colourbatch based on PS matrix, was used in the research. The variable processing parameters were: injection temperature T_{wv} , volume flow rate V_{wv} , residence time and the addition of a colourbatch. On the basis of the measurements, it was found that the processing conditions and the addition of the colourbatch have low effect on the hardness of the mouldings, which was in the range from 75.59° Sh D (Shore type D) to 81.95° Sh D. It was also noted that the addition of colourbatch with TiO_2 and increasing injection temperature reduces impact strength even by several dozen percent. Moreover, it was found that use of TiO_2 causes a delay in the ignitability of the samples in selected cases. It is difficult to determine whether the variable processing conditions or the addition of TiO_2 on the PS matrix have a greater impact on the ignitability of the moulded parts.

Keywords: injection moulding; ABS; PS; TiO_2 ; flame retardant; mechanical properties

1. Introduction

One of the most frequently used engineering polymer is acrylonitrile-butadiene-styrene (ABS). This is due to its good mechanical properties, chemical resistance, easy processing, good surface quality of ABS parts, possibility of use in advanced applications, as well as good quality-price correlation [1-11]. ABS is used in various branches, such as: automotive, electrical or electronic [6-9]. Despite its many advantages, ABS is characterized by high flammability related to its chemical structure. Toxic gases produced during combustion can limit the wider use of ABS. These drawbacks also necessitate regular flammability testing of ABS products. Therefore, its modifications aimed at reducing flammability, seem not only a big challenge, but also a necessity [11-18]. One of the methods of reducing the flammability of polymers is use of flame retardants [3,18,19]. ABS has been successfully modified with halogen-containing compounds [3,18-26]. However, their use has been limited due to environmental and public safety concerns – large amounts of

toxic and corrosive fumes were generated during combustion. Therefore, halogen – free flame retardants are becoming more and more popular [27-32]. An interesting solution is use of the modifiers that are flame retardants at the same time. An example of such substance is titanium dioxide TiO_2 . It is a white, odourless, non-toxic, non-flammable mineral with good optical and chemical properties, good thermal and UV resistance and a low price [33-48]. It is used in the food, cosmetic, pharmaceutical, paper, textile and polymer processing industries [49-54]. Many studies have shown the effect of addition of TiO_2 , to impregnates or coatings, on reducing flammability [49-51,54-56]. Despite numerous studies on the use of TiO_2 as an insulating agent, there are still no publications concerning use of titanium white both: as a colouring agent and as a flame retardant for engineering thermoplastics.

The aim of the study was to determine the effect of processing conditions and the addition of a colourbatch on the PS matrix on selected functional properties of mouldings such as: flammability, colour and gloss, as well as mechanical properties

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of mouldings such as: hardness determined by the Shore D method and impact strength determined by the Charpy with notch method. The research compared samples made of ABS with and without colourbatch. Test results obtained for the mouldings made of ABS with addition of flame retardant based on ABS matrix are presented in the paper [57].

2. Research material and methods

ABS (acrylonitrile-butadiene-styrene) copolymer under trade name Terluran GP 35 Natur, intended for injection, was used for the research. As flame retardant was used a colourbatch (concentrate) containing white pigment – titanium dioxide (TiO_2) – based on PS Empera 662 N matrix (mass fraction of the pigment powder was 20%). The concentrate was dosed in the amount of 3% (mass fraction). The polymer and concentrate were not dried as they were stored in sealed, original bags.

Samples, in the shape of A-type tensile bars, were made according to the standard [58], on a KM65 – 160 C4 injection moulding machine by Krauss-Maffei. Mouldings were made in various processing conditions, according to the research plan (TABLE 1). Processing parameters were selected based on the manufacturer's recommendations and literature [59]. The remaining injection parameters were as follows:

- mould temperature $T_f = 50^\circ\text{C}$,
- holding time $t_d = 20$ s,
- cooling time $t_c = 20$ s,
- injection pressure $p_w = 100$ MPa,
- holding pressure $p_d = 60$ MPa.

TABLE 1

Research plan

Series	Residence time [s]	Injection temperature T_w [$^\circ\text{C}$]	Volume flow rate V_w [cm^3/s]	Colourbatch [%]
1	1	260	25	0
				3
2	1	280	25	0
				3
3	1	260	85	0
				3
4	1	280	85	0
				3
5	20	260	25	0
				3
6	20	280	25	0
				3
7	20	260	85	0
				3
8	20	280	85	0
				3

Obtained mouldings were earmarked for further research such as: gloss, colour, flammability, hardness and impact strength.

3. Results of experiments

3.1. Gloss and colour

Gloss measurements were taken with glossmeter Elcometer 406, according to standard [60]. Initial gloss tests were carried out at an angle of incidence of light on the mouldings surface (geometry) of 60° . Gloss of the mouldings was determined on the basis of the Gloss Units (GU) value. Depending on the obtained results, additional measurements are made with a geometry of 20° (when the gloss value is >70 GU) or with a geometry of 85° (when the gloss is <10 GU). Samples in the form of cuboids (dimensions of $150 \times 23 \times 4$ mm) were made in accordance with the research plan (TABLE 1). The gloss was measured at three measuring points on the surface of each moulding, numbered consecutively in the direction of the material flow at a distance of 37.5, 75, 112.5 mm from the gate. Results are presented in TABLE 2.

For samples made of undyed ABS, it was found that the mouldings produced at a low injection temperature of 260°C and a high volume flow rate had the highest gloss (series 3, 67.54 GU). On the other hand, the lowest gloss value was noticed for mouldings manufactured in series 7 (54.19 GU). It was found that increasing residence time to 20 s contributes to a lower gloss degree from 3% (for series 4 and 8) to 19% (for series 3 and 7).

The addition of colourbatch on the PS matrix contributes to a change in the gloss value. The highest value was noticed for mouldings from series 8 (61.23 GU), and the lowest for series 6 (43.90 GU). The increased injection temperature to 280°C and a low volume flow rate ($25 \text{ cm}^3/\text{s}$) contributed to obtaining a surface with a lower gloss. In turn, increasing the volume flow rate to $85 \text{ cm}^3/\text{s}$ contributed to a higher gloss value by 3-4 GU. The simultaneous increase of the volume flow rate and residence time to 20 s resulted in an increase in the gloss degree by 6-7% (series 3 and 7 as well as 4 and 8).

The colour tests were carried out by the X-rite SP 60 spherical spectrophotometer. Measurements were made on five mouldings from each series, at 3 points on the surface of samples, in the direction of the material flow in the cavity. Colour was determined by the CIE *Lab* model, where *L* is luminance (brightness, black to white), *a* determines the colour from green to purple, and *b* the colour from blue to yellow. The obtained results were averaged and summarized in TABLE 2.

Undyed ABS has a milky white colour, while the colouring agent (colourbatch) can be described as the so-called snow white. The addition of colourbatch increases the luminance *L* from $10 \text{ cd}/\text{m}^2$ (for series 2) to $16 \text{ cd}/\text{m}^2$ (for series 7).

Undyed ABS samples are characterized by luminance *L* ranging from 79.07 to $84.88 \text{ cd}/\text{m}^2$, however, it is difficult to clearly indicate the relationship between changes in processing parameters and the luminance *L* of the mouldings. On the other hand, dyed mouldings are characterized by a luminance *L*, changing in a narrow range from $94.51 \text{ cd}/\text{m}^2$ to $95.34 \text{ cd}/\text{m}^2$. Also in this case, it is difficult to indicate a relationship between the processing conditions and obtained values.

TABLE 2

Results of measurement of gloss and colour

Series	Residence time [s]	Injection temperature T_w [°C]	Volume flow rate V_w [cm ³ /s]	Colourbatch [%]	Colour			Gloss [GU]
					L [cd/m ²]	a [-]	b [-]	
1	1	260	25	0	79,93	-3,36	2,35	61,72
				3	95,11	-1,13	6,94	56,03
2	1	280	25	0	84,88	-4,35	1,82	66,31
				3	95,18	-1,12	7,06	49,80
3	1	260	85	0	82,36	-4,20	3,54	67,54
				3	95,34	-1,03	6,59	54,03
4	1	280	85	0	80,96	-3,99	3,21	60,10
				3	95,28	-1,07	6,87	57,13
5	20	260	25	0	79,88	-4,25	5,21	57,90
				3	94,51	-1,36	8,01	48,73
6	20	280	25	0	79,56	-3,57	4,59	55,81
				3	94,70	-1,30	7,96	43,90
7	20	260	85	0	79,07	-3,48	5,34	54,19
				3	95,17	-1,08	6,73	57,30
8	20	280	85	0	79,45	-4,01	4,98	58,28
				3	95,04	-1,16	7,28	61,23

For mouldings without colourbatch the value of the parameter *a* is in the “green” part of the CIE *Lab* system. Due to the addition of the colourbatch, it is moved towards the centre of the system, but still remains in the “green” part. For changes in *a* value, it is difficult to determine the unequivocal influence of processing conditions. The value of parameter *b* for non-dyed ABS mouldings is located closer to the centre of the CIE *Lab* system, in the “yellow” part. The addition of colourbatch increased the value of this parameter and its further shift towards the yellow colour. Changes in the processing conditions (i.e. increased injection temperature and volume flow rate) resulted in a decrease in the *b* value in selected cases and its shift towards the beginning of the CIE *Lab* system.

3.2. Flammability

Another research was the flammability test by UL 94-5VA [61], which allows to determine the flammability class of the material. The results are shown in Fig. 1, where ABS means

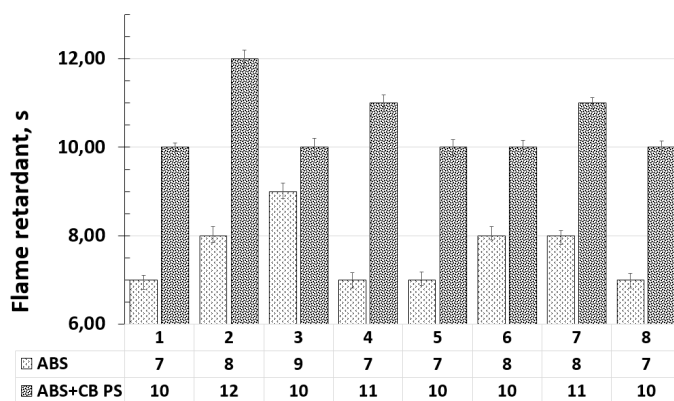


Fig. 1. Flame retardant of mouldings with and without colourbatch

samples made of undyed ABS and ABS+CB PS means mouldings with the addition of colourbatch on the PS matrix.

Analysing the obtained results of flammability tests, it was noticed that the addition of colourbatch with TiO₂ delays ignition of samples by approx. 25 s. The undyed ABS samples ignited after 10 s, and the dyed ones after 35-37 s. Cotton placed under undyed samples burns after 7 to 9 s, regardless of the conditions in which the mouldings were produced. In turn, for samples made of ABS with addition of colourbatch, this time was between 10 s to 12 s. Major change was noticed for series 2 (from 8 to 12 s) and for series 4 (from 7 to 11 s). Moreover, for dyed ABS mouldings, it was found that samples produced with a low residence time and a higher mould temperature $T_f = 280^\circ\text{C}$ burn longer. Undyed mouldings can be classified to the V1 flammability class. In turn, ABS mouldings with flame retardant (containing TiO₂) on PS matrix addition, can be classified to V0 flammability class.

3.3. Hardness and impact strength

The hardness tests were made with Shore type D hardness tester, according to the standard [62]. Hardness was determined at five measuring points on the surface of each sample, numbered consecutively in the direction of material flow in the cavity. In the hardness tests 10 repetitions were made. Differences in hardness between individual measuring points did not exceed 0.3-0.4° Sh D, therefore these values were averaged for further calculations. The arithmetic mean was calculated for the undyed mouldings and for the mouldings with flame retardant containing TiO₂ on the PS matrix. The results of hardness measurements are presented in Fig. 2.

Analysing the influence of processing conditions, it was found that samples made of ABS with 3% of colourbatch

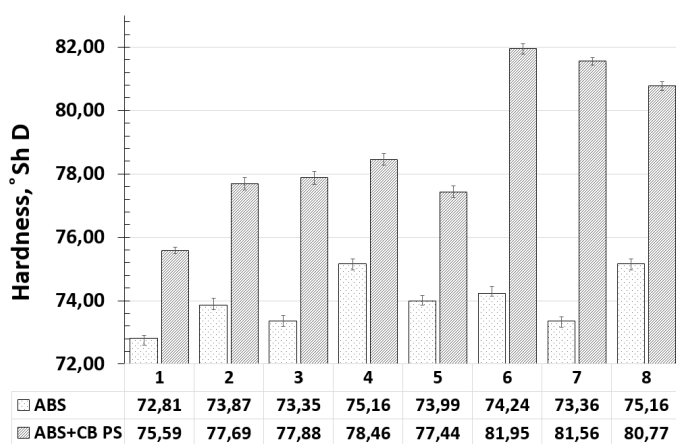


Fig. 2. Results of measurement of hardness

(series 6) had the highest hardness (81.95° Sh D) and the smallest hardness (72.81° Sh D) had samples made of pure ABS from series 1. The addition of a flame retardant, regardless of the processing conditions, increased the hardness by about 4% to 9.5%.

For undyed ABS mouldings, it was observed that increasing injection temperature T_w from 260°C to 280°C, in all cases, resulted in increase of hardness. Also, the increased residence time to 20 s (series 5 ÷ 8) and low volume flow rate $V_w = 25 \text{ cm}^3/\text{s}$, in most cases, contributed to the increase in hardness. Increasing V_w did not change the mouldings hardness.

Similar trends were observed in most cases for mouldings made of ABS with the addition of colourbatch.

For the impact strength tests, bars were cut out of the tensile bars. Then, with a knife, an A-notch was incised in the prepared samples. 10 repetitions were used. Tests were made according to the standard [63]. The results of the measurements of the impact strength of mouldings without and with the addition of a colourbatch are presented in Fig. 3.

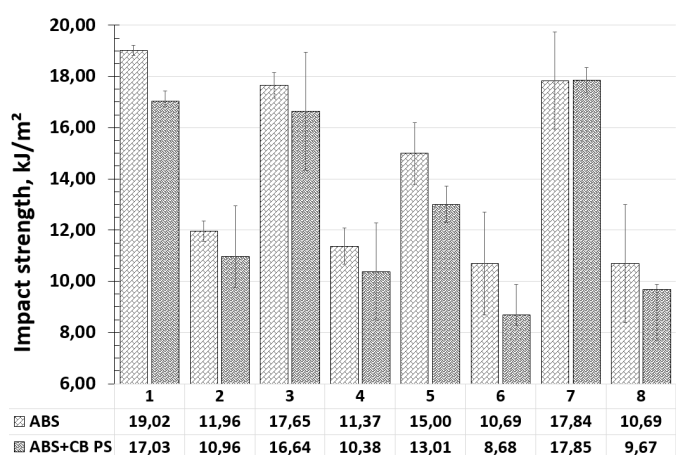


Fig. 3. Results of measurement of impact strength

It was found that the addition of colourbatch contributed, in most cases, to the reduction of the impact strength of the produced mouldings. The impact strength value decreased by 0.1% to 18.9% after application of the flame retardant. The lowest

value (8.68 kJ/m²) was noticed for samples made of coloured ABS in series 6 – with high $T_w = 280^\circ\text{C}$, low $V_w = 25 \text{ cm}^3/\text{s}$ and residence time 20 s.

On the other hand, the highest impact strength was characteristic for mouldings made of undyed polymer produced in series 1 (19.02 kJ/m²).

For non-dyed ABS mouldings, it was found that in most cases, increasing residence time to 20 s contributes to reduction in impact strength (e.g. series 1 and 5). Increasing volume flow rate to 85 cm³/s with the simultaneous low injection temperature ($T_w = 260^\circ\text{C}$) allows to obtain high impact strength values (series 3 and 7). Increasing injection temperature while maintaining a high V_w reduces the impact strength.

For mouldings made of ABS with flame retardant, it was noted that the highest impact strength was characteristic for the samples produced at low T_w and low V_w . Change in the residence time to 20 s also contributed to the reduction of the impact strength value. The higher injection temperature results in the lowest impact strength of the obtained samples.

4. Conclusions

The conducted research allowed to conclude that the addition of colourbatch on a matrix made of a material other than the base material (but still from the same group) containing titanium white TiO₂ allows not only to obtain a whiter colour of the mouldings, but also changes the properties of the mouldings.

It was found that the processing conditions did not affect the flammability changes of the obtained samples. Addition of colourbatch/flame retardant based on the PS matrix containing TiO₂ contributed to the extension the ignition time of the samples and allowed to change its flammability class to V0. Authors of articles [64,65] described structural changes caused by the addition of TiO₂.

Addition of colourbatch contributed also to the reduction of gloss in most cases, e.g. by 13% for series 1 and 5. It was found that increasing residence time to 20 s contributes to a lower gloss degree for mouldings made of undyed ABS. But for dyed ABS mouldings simultaneous increase of volume flow rate and residence time to 20 s resulted in an increase in the gloss degree by 6-7%.

For undyed samples it is difficult to clearly indicate the relationship between changes in processing parameters and the luminance L of the mouldings but in the selected cases it was found, that increase of the injection temperature allow to obtain whiter samples. Simultaneous increase in the volume flow rate and extension of residence time reduces mouldings luminance L . A similar tendency was found for mouldings made of coloured ABS.

The addition of flame retardant/colourbatch allows to obtain whiter samples but also leads to changes in the a and b values. It causes their values to shift towards the beginning of the CIE Lab system. For undyed samples, changes in the processing conditions (i.e. increased injection temperature and volume flow

rate) resulted in a decrease in the b value in selected cases and its shift towards the origin of the CIE *Lab* system. It is difficult to determine trends for the parameter a .

Addition of colourbatch contributed to the reduction of impact strength by over 18% for selected series and at the same time, it increase mouldings hardness by up to 10% in selected cases. It can be noticed that changes in processing conditions do not significantly affect changes in mechanical and functional properties of samples. Shown changes may depend not only on content of the TiO₂ in flame retardant, but also on the PS matrix of colourbatch. Increasing proportion of styrene phase in the copolymer may also influence the observed changes. At the same time changes can be connected with form of titanium white. Titanium dioxide occurs naturally in three forms: anatase, rutile and brookite, however, for commercial use it is modified. So it is difficult to determine whether the results are influenced only by titanium white or also by the substances used to modify it.

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