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Processing Conditions vs. Selected Properties of Mouldings Made of ABS with Addition of Flame Retardant

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The scope of application of polymers is gradually expanding, thanks to the possibility of their modification. The most common choice is dyeing. Regardless of the color of the used coloring agent, titanium white is always applied. It gives white color or is used as an optical brightener. At the same time, TiO₂ is recommended as a flame retardant. It is mostly used in the form of a pigment (powder). However, there are no studies where TiO₂ is used as a colorbatch. The aim of this work was to investigate the effect of titanium dioxide in the form of a colorbatch on the flammability and selected properties of mouldings manufactured in various processing conditions. A colorbatch on an ABS matrix was used in the research. The variable processing conditions were: injection temperature T_w , volume flow rate V_w , plasticization delay and the addition of the colorbatch. It was found that the processing conditions and the addition of the colorbatch did not have a significant effect on the hardness, which was in the range from 72.81°Sh (Shore) to 75.95°Sh (Shore). It was also noted that the addition of a colorbatch and increasing T_w reduces the impact strength even by several dozen percent. Moreover, it was noted that use of the colorbatch with TiO₂ 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 the colorbatch have a greater impact on the ignitability of the mouldings.

topics: injection moulding, ABS, TiO₂, flame retardant

1. Introduction

The use of polymers has increased due to the possibility of their dyeing. One of the most common colorants is the inorganic titanium dioxide pigment TiO₂. It is a white, non-transparent, odorless, porous mineral that occurs naturally in three forms: anatase, rutile and brookite, however, it is modified for commercial use [1-5]. TiO₂ has good optical properties and high ultraviolet protection, antiseptic properties, good chemical stability and a low price [6–14]. It is used in the plastics industry, paint production, pharmaceuticals, cosmetics, food, paper, textiles and civil engineering. Due to its properties, depending on the used form and thermal stability, TiO₂ is used in solar cells, biosensors or thermoelectric equipment [12–15]. Moreover, it has been found that the use of titanium dioxide as a component of the impregnating layer improves fire resistance of wood [16, 17]. It also significantly improves fire resistance as a component of coatings [18], and may even be an alternative to the previously used flame retardants in the production of refractory materials [19–21]. Despite numerous studies on the use of TiO_2 (mainly a component of coatings) as an insulating agent, there are still no publications concerning the use of titanium white both as a coloring agent and as a flame retardant for engineering thermoplastics.

The aim of this research was to evaluate the effect of processing parameters and the addition of a colorbatch on an ABS matrix on basic mechanical properties such as: hardness determined by the Shore type D method, the impact strength determined by the Charpy with the notch method and functional properties such as flammability, color and gloss of mouldings made of undyed and dyed ABS.

2. Materials and research methods

Acrylonitrile-butadiene-styrene (ABS) by BASF under the trade name Terluran GP 35 Natur was used for the tests. As a flame retardant, a coloring agent containing titanium dioxide (TiO₂) in the form of a colorbatch on an ABS matrix was used (the mass fraction of TiO₂ was 20%). The concentrate was dosed in the amount of 3% (mass fraction). ABS and the concentrate were not pre-dried as they were stored in sealed, original bags. The test specimens, in the shape of A-type tensile bars in accordance with the standard [22], were made on a KM65-160 C4 injection

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Research	plan.
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TABLE I

Series	Plasticization delay [s]	Injection Injection		Colorbatab	
		temperature	velocity	10/1	
		$T_w \ [^{\circ}C]$	$V_w ~[{ m cm}^3/{ m s}]$	[70]	
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	

moulding machine by Krauss–Maffei. The mouldings were produced under various injection conditions according to the research plan (Table I). The remaining injection parameters were as follows: mould temperature $T_f = 50$ °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. The processing parameters were selected on the basis of the producer's recommendations and by H. Zawistowski et al. [23].

The hardness tests were performed using a Shore type D hardness tester in accordance with the standard [24]. The hardness was determined at five measuring points on the surface of each part, numbered sequentially in the direction of material flow in the cavity. Ten repetitions were used in the tests. Differences in hardness between the individual measuring points did not exceed 0.4°Sh D, therefore these values were averaged for further calculations. The arithmetic mean was calculated for the undyed and dyed mouldings. In turn, for impact tests, bars were cut from the tensile bars, and then an A-notch was incised in the samples. Charpy impact tests, with the use of a 1 J hammer, were performed in accordance with the standard [25]. Ten replicates were used in the impact tests. Another test was the measurement of the gloss with an Elcometer 406 Glossmeter in accordance with the standard [26]. Basic gloss tests were performed at an angle of light incidence of 60°. Depending on the obtained results, additional measurements may be made with a geometry of 20° (gloss value is < 70 GU) or with a geometry of 85° (gloss is < 70 GU). The gloss was assessed on the basis of the value of the Gloss Units. Samples in the form of cuboids with dimensions of $150 \times 23 \times 4 \text{ mm}^3$ were made in accordance with the research plan (Table I). The gloss was measured at three points on the surface of each part, numbered sequentially in the direction of material flow. Results were presented in Table II.

Results of measurement of	of selected p	properties.
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	Colorbatch	Color			Gloss	Flame
Series	[%]	$L \ [cd/m^2]$	a	b	[GU]	retarded [s]
1	0	79.93	-3.36	2.35	61.72	7
	3	95.42	-1.04	6.67	49.66	10
2	0	84.88	-4.35	1.82	66.31	8
	3	95.39	-1.09	6.85	45.16	8
3	0	82.36	-4.20	3.54	67.54	9
	3	95.34	-1.12	6.89	47.00	9
4	0	80.96	-3.99	3.21	60.10	7
	3	95.40	-1.06	6.61	39.43	9
5	0	79.56	-4.25	5.21	57.90	7
	3	95.05	-1.20	7.28	24.93	13
6	0	79.56	-3.57	4.59	55.81	8
	3	95.01	-1.25	7.86	23.03	12
7	0	79.07	-3.48	5.34	54.19	8
	3	95.29	-1.23	7.27	15.40	11
8	0	79.45	-4.01	4.98	58.28	7
	3	95.42	-1.13	7.07	38.43	11
	3					

The color tests were carried out with the use of a spherical spectrophotometer SP60 by X-rite. Measurements were made on five samples from each series, at three points on the surface of the moulded part, in the direction of the material flow. The color was determined using a CIE Lab independent model where L is luminance (brightness, black to white), a denotes green to purple, and b denotes a color from blue to yellow. The obtained results were averaged. The last to perform was the flammability test by the UL 94-5VA method [27], which allows to determine the flammability class of the material.

3. Research output

The results of hardness measurements of the mouldings are shown in Fig. 1 (ABS means samples made of undyed ABS and ABS+CB ABS means dyed ones).

It was found that samples made of ABS with the addition of 3% of the colorbatch, produced in series 6, had the highest hardness $(75.95^{\circ}Sh D)$. The lowest hardness $(72.81^{\circ}Sh D)$ was noted for mouldings from series 1. The addition of the coloring agent, regardless of the processing conditions, increased the hardness by about 0.63% to 3%. For mouldings made of undyed ABS, it was observed that increasing injection temperature T_w to 280 °C in all cases resulted in an increase in hardness. Also, increasing the plasticization delay to 20 s (series 5–8) and the low volume flow rate $V_w = 25 \text{ cm}^3/\text{s}$ usually contributed to the increase in hardness. In turn, increasing V_w did not change the hardness. Similar trends were observed for mouldings made of ABS with the colorbatch addition.

The results of the measurements of the impact strength of mouldings undyed and dyed are presented in Fig. 2. It can be seen that the addition of the colorbatch generally contributed to



Fig. 1. Results of hardness measurements.



Fig. 2. Results of impact strength measurements.

the reduction of the impact strength. The impact strength value was reduced by 23% to 37% after the application of the colorbatch. The exception are mouldings from series 5, where a slight increase was noted. The lowest value (6.08 kJ/m²) was found for samples made of colored ABS, in series 6 — made with high $T_w = 280$ °C, low $V_w = 25$ cm³/s and plasticization delay of 20 s. The highest impact strength was characteristic for the mouldings made of undyed ABS manufactured in series 1.

For undyed mouldings, it was found that in most cases, extending the plasticization delay to 20 s contributed to the reduction of the impact strength (e.g., series 1 or 5). But increasing the V_w to 85 cm³/s with the simultaneous use of a low $T_w = 260 \,^{\circ}\text{C}$ allows to obtain samples with a high value of the impact strength (series 3 and 7). Increasing T_w , while maintaining high V_w , reduces the impact strength. For mouldings made of ABS with the addition of the colorbatch, it was noted that the highest impact strength was characteristic for samples made at low T_w and low V_w . Change in the plasticization delay time to 20 s also contributed to the reduction of the impact strength. By using a higher V_w and a higher T_w , samples with a lower impact strength are produced.

The results of the gloss and color tests were presented in Table II. For samples made of undyed ABS, it was found that mouldings produced at low T_w and high V_w had the highest gloss (series 3; 67.54 GU). The lowest gloss was noticed for the mouldings manufactured in series 7 (54.19 GU). Extending the plasticization delay to 20 s results in a lower gloss of the surface. The addition of the colorbatch reduces the gloss, in some cases by up to 30% (e.g., series 7). The highest value was obtained for mouldings from series 1 (49.66 GU), and the lowest — for series 7 (16.40 GU). Also extending the plasticization delay to 20 s contributed to a lower gloss. Increasing the T_w to 280 °C, mostly, reduces the gloss.

In the case of color tests, it should be noted that undyed ABS has a milky white color, while the coloring agent can be described as the so-called "snow white." The addition of the colorbatch contributes to an increase in L luminance (up to 17%, series 1). Samples from virgin ABS are characterized by luminance L ranging from 79.07 to 84.88 cd/m^2 , however, it is difficult to indicate trends between changes in the processing parameters and the luminance L. All moulded parts made of colored ABS have a similar luminance L (about 95 cd/m²), regardless of the processing conditions. For the parameter a, it was found that for undyed mouldings, its value is in the "green" part of the CIE Lab system. Due to the addition of the colorbatch, it is moved towards the center of the array, although it still remains in the "green" part. The value of parameter b for samples made of undyed ABS is located closer to the center of the CIE Lab system, in the "yellow" part. The addition of the colorbatch shifted it towards yellow.

During the flammability test, it was noticed that the addition of the colorbatch with TiO_2 delayed the ignition of the samples by about 20 s. Samples made of virgin ABS ignited after 10 s, and those from dved ABS — after 30 s. Cotton placed under the undved samples burns after 7 to 9 s, regardless of the processing conditions. In turn, for samples made of ABS with the colorbatch addition, this time was between 9 and 13 s. The biggest change (from 7 to 13 s) was found for series 5. Moreover, for mouldings made of colored ABS, it was found that samples produced in a plasticization delay of 20 s burn longer. Samples made of undyed ABS can be qualified to the V-2 flammability class. The addition of the colorbatch allows to obtain samples of the higher V-1 class.

4. Conclusions

On the basis of research it was noticed that the addition of the colorbatch containing TiO_2 allows to obtain a whiter color but also changes the properties of the samples. It may be due to the porous structure of pigment TiO_2 contained in the colorbatch. The addition of the colorbatch increased the hardness of mouldings, but at the same time, reduced the impact strength and gloss. It also caused an increase in the ignition time and allowed to include the samples in the V-1 flammability class.

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