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MECHANICAL PROPERTIES MODIFYING OF A NON-FLAMMABLE POLYMER MIXTURE

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S u m m a r y

In order to modify the non-flammable HIPS/ $Mg(OH)_2$ mixture, the admixture of a synergic system consisting of antimonium trioxide and hexacyclobromododecane was introduced. The purpose of the work was to find whether in such case, that is at the lower amount of the basic mineral flame retardant it would be possible to improve both mechanical and flame properties. Also the effect of introducing thermoplastic elastomers as the impact strength modifier is presented in this paper.

Keywords: mechanical and flame properties, polymer mixture, high-impact polystyrene,

Modyfikacje właściwości mechanicznych trudnopalnej mieszaniny plimerowej

S t r e s z c z e n i e

W pracy opisano modyfikowanie właściwości mechanicznych oraz palnych materiału HIPS/$Mg(OH)_2$ (polistyren wysokoudarowy/wodorotlenek magnezu) przez wprowadzenie do ich mieszaniny układu synergicznego – trójtlenku Sb_2O_3 i środka CD-75P (hexacyclobromododecane). Celem było zmniejszenie zawartości $Mg(OH)_2$, który znacząco wpływa na pogorszenie właściwości mechanicznych badanego materialu HIPS/$Mg(OH)_2$ z zachowaniem akceptowalnego poziomu właściwości palno-dymowych. Dodatkowo podczas modyfikowania właściwości mechanicznych (głównie udarności) wprowadzono do materiału HIPS/$Mg(OH)_2$ niewielkie dodatki elastomerów termoplastycznych.

Słowa kluczowe: właściwości mechaniczne, właściwości palno-dymowe, mieszanina polimerów, polistyren o dużej plastyczności

1. Introduction

Mineral flame retardants have to be used in large quantities in order to make polymer materials non-flammable which, in turn, worsens all mechanical properties of the final product [1, 2].

The performance of the mineral flame retardants is based on the endothermal decomposition which is accompanied by emission of water and a metal oxide. The water turns into steam thus lowering the flame temperature while the metal oxide forms a thin layer which separates the flame from the material surface. Both these phenomena slow down the decomposition process [2-4].

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As was mentioned above, large amounts of the filler is responsible for the deterioration of mechanical properties. That is why the material should undergo further modification. In the course of the work performed at The Plastics Processing Division of The Warsaw University of Technology a non-flammable mixture containing 55% of the filler was obtained. In the previous papers [5-7] it was found that an essential modification of the mechanical properties of the material was necessary, preferably by the admixture of the thermoplastic elastomer - SBS (triblock Styrene-Butadiene-Styrene copolymer). The results were not fully satisfying which led to the conclusion that lowering the amount of the filler at simultaneous admixing a synergic system of halogen compounds plus replacing SBS by SEBS (Styrene-Ethylene-Butylene-Styrene) elastomer might help obtain a valuable non-flammable polymer [8-10].

In the paper [5], the results of primary modification of high impact polystyrene (HIPS) by the introduction of magnesium hydroxide were presented. After testing the properties of the material it was found that the improvment of mechanical strength was neccesary as all mechanical properties dropped due to the ammount of the flame retardant used [2, 5, 9]. Consequently new admixtures were introduced to the two-component system (HIPS plus $Mg(OH)_2$) to strenghten the material [9-12].

2. Materials used

2.1. Impact polystyrene

Commercial polystyrene Owispol 825 manufactured by Dwory S.A.,Poland was used. It is obtained in the continuous process of bulk polymerization from styrene and butadiene and it is intended for the injection moulding. It can be used for manufacturing popular household articles, toys, office items etc. Its feature is a glossy surface. The melt flow index MFI is 6-9 g/10 min (200°C, 5 kg), the Vicat softening point is 89°C (1 kg, 50ºC/h), the impact strength is 45-55 kJ/m^2, the oxygen index OI – 18.5%.

2.2. Mineral flame retardant

Magnesium hydroxide $Mg(OH)_2$ manufactured by Martinswerk GmbH under the commercial name Magnifin H5 was used as mineral flame retardant. It dampens smoke effectively and is thermally stable at the temperature up to 340°C. It does not release any toxic or corrosive fumes. If added to plastics which emit acidic substances during burning, it decreases their concentration or neutralizes them. It is also an effective thermal stabilizer if used together with the traditional halogen flame retardants.

2.3. SBS thermoplastic elastomer

In order to improve the impact strength of the HIPS/$Mg(OH)_2$ mixture, a triblock SBS (styrene-butadiene-styrene) thermoplastic elastomer was introduced. It is the product of Atofina commercially available as Finaclear 530 . This material features good mechanical and thermal properties and can be easily injection moulded or extruded. SBS is used both as a basic material and as a modifier of impact strength of other plastics including HIPS.

2.4. SEBS thermoplastic elastomer

The next modifier of impact strength used in this work was also a thermoplastic elastomer. It is styrene-ethylene-butylene-styrene copolymer and it has a block structure based on the flexible ethytene-butylene block in the middle with the attached rigid styrene blocks at both ends (the same as in the case of SBS). Such structure forms a two-phase system characterized by two different glass transition points: 95°C for polystyrene and -50°C for poly (ethylene-butylene). Polystyrene blocks join one another thus creating domains which build up the so called physical crosslinking. In this way a reinforced, elastic structure is obtained which is typical of vulcanized rubber and other crosslinked elastomers. During heating the material above the glass transition point of polystyrene, the domains soften and allow for flow under pressure. This process is, however, reversible and when the material is quenched, the 3D crosslinks build up again. At very low temperature the material remains flexible until the glass transition point of poly(ethylene-butylene) is reached. The product used in this work is manufactured by TCT.

2.5. Halogen flame retardant

As an organic flame retardant, hexacyclobromododecane $C_{12}H_{18}Br_6$ was used. It is manufactured by Great Lakes and designated as CD-75P. It is the only bromium-based flame retardant which, in spite of its toxic features, is permitted to use if no other substances can be applied.

This compound contains 74.7% bromium and features good thermal stability (up to 263°C) and low water absorption. Its softening point is 182-192°C.

2.6. Antimony trioxide

In order to improve the effectiveness of the mentioned hexacyclo-bromododecane (CD-75P), it was introduced together with antimony trioxide. Thus those two compounds (CD-75P) plus antimony trioxide formed a synergic system. The compound used is the product of Great Lakes and is sold under the name Timonox Blue Star TMS-HP. It is a white powder of the particles size 0.3-0.9 µm. Its softening point is 655°C.

3. Modifying the mixture by means of halogen synergic system

In this part of the work the synergic system of antimony trioxide and hexacyclobromododecane was introduced into the non-flammable mixture prepared previously [4]. The purpose was to check whether in such case, that is at lower amount of the mineral filler, it would be possible to improve both flame and mechanical properties.

The following sets of mixtures were prepared:

1. 45% $Mg(OH)_2$, 30% HIPS, 20% SBS, 2,5%, Sb_2O_3, 2,5% CD-75P
2. 50% $Mg(OH)_2$, 22,5% HIPS, 22,5% SBS, 2,5%, Sb_2O_3, 2,5% CD-75P
3. 52% $Mg(OH)_2$, 22% HIPS, 20% SBS, 3%, Sb_2O_3, 3% CD-75P
4. 40% $Mg(OH)_2$, 25% HIPS, 25% SBS, 5%, Sb_2O_3, 5% CD-75P

As a next step the samples for mechanical and flame tests were injection moulded. Table 1 presents the results of testing the mechanical parameters. It can be seen that, in spite of the decreased amount of the mineral filler, both impact strength and the other parameters remained at the same low level (compare paper [5]).

In Table 2 the results of flame and smoke tests are presented. The synergic halogen system was supposed to cause an essential increase of the flame properties. The results showed, however, that the oxygen index rose slightly but remained under the minimum required level 28%. The other two parameters (exposure S and illumination intensity E4[1] dropped meaningfully which means higher smoke emission. For set 4 in Table 2, that is for the highest content of the synergic system, the illumination intensity was only 10,5 lx even though the oxygen index was relatively high (yet below 28).

Table 1. Mechanical properties of the non-flammable mixture with the admixture of synergic system

Set	Filler content, %					Mechanical properties			
	$Mg(OH)_2$	HIPS	SBS	Sb_2O_3	CD-75P	Hardness $HK_{5,30}$ MPa	Impact Strength KJ/m^2	Tensile Strength MPa	Young Moduls MPa
1	45,0	30,0	20,0	2,5	2,5	69,4	4,3	17,4	3423,0
2	50,0	22,5	22,5	2,5	2,5	80,1	4,6	17,0	3973,0
3	52,0	22,0	20,0	3,0	3,0	82,6	3,8	15,8	3703,0
4	40,0	25,0	25,0	5,0	5,0	78,0	4,4	17,4	3250,0

Concluding this series of tests it can be said that application of the synergic halogen system treated as the admixture to the basic mineral flame retardant gave

[1] These two parameters represent smoke emission. They are measured in a standardized chamber in which smoke passes between a source of light and a photo-cell. The less smoke, the more light is absorbed by the photo-cell. Consequently, high values of both S and E4 are desired.

no positive results. Neither mechanical nor smoke properties were improved. A higher content of the synergic system might possibly rise oxygen index above the minimum required 28% but the emission of smoke would probably be so high that the material would be rejected as dangerous.

Table 2. Flame and smoke properties of the non-flammable mixture with the admixture of synergic system

Set	**Filler content, %**					**Flame and smoke parametres**		
	$Mg(OH)_2$	**HIPS**	**SBS**	**Sb_2O_3**	**CD-75P**	Oxygen Index %	Exposure *lxs*	Illumination intensity *Lx*
1	45,0	30,0	20,0	2,5	2,5	23,0	12570,0	27,3
2	50,0	22,5	22,5	2,5	2,5	25,7	16409,0	45,9
3	52,0	22,0	20,0	3,0	3,0	26,5	16892,0	45,1
4	40,0	25,0	25,0	5,0	5,0	26,0	10529,0	10,5

4. Modifying the mixture by means of thermoplastic sebs elastomer (styrene- ethylene- butylene- styrene)

In the next part of the work the SBS elastomer was replaced by a less flammable one-namely by the SEBS. It is chemically familiar with the SBS previously used. It contains ethylene-butylene group instead of butadiene. Pure SEBS emits very little smoke when burning. Illumination E4 is 62.8 lx and exposure is 20608 lxs. Oxygen index is, however, low (19%) which is close to the one for SBS and which is unsatisfactory.

The purpose of introducing SEBS was the further improvement of impact strength. This material is more flexible than SBS due to more flexible segments in the macromolecule. This is why it was expected to improve essentially the impact strength of the mixture.

Four sets of mixtures containing SEBS were prepared:

5. 55% $Mg(OH)_2$, 30% HIPS, 15% SEBS
6. 55% $Mg(OH)_2$, 40% HIPS, 5% SEBS
7. 55% $Mg(OH)_2$, 31% HIPS, 14% SEBS
8. 55% $Mg(OH)_2$, 22,5% HIPS, 22,5% SEBS

Next, as it was done previously, mechanical and flame properties were tested. Table 3. presents the mechanical properties.

Table 3. Mechanical properties of the non-flammable mixture with the admixture of styrene-ethylene-butylene-styrene (SEBS)

	Filler content, %			Mechanical properties			
Set	**$Mg(OH)_2$**	**HIPS**	**SEBS**	**Hardness $HK_{5,30}$ MPa**	**Impact Strength KJ/m^2**	**Tensile Strength MPa**	**Young Moduls MPa**
5	55,0	30,0	15,0	79,60	3,95	11,4	3697,4
6	55,0	40,0	5,0	68,90	3,87	12,2	3712,8
7	55,0	31,0	14,0	61,90	4,4	11,1	3488,1
8	55,0	22,5	22,5	66,50	4,5	10,4	3444,3

With the increased content of SEBS, hardness dropped a bit (Table 3 and Fig. 1) yet remaining at the satisfactory level. The other mechanical parameters were only slightly improved (Fig. 2-4). The SEBS was expected to improve the mechanical properties much more than SBS but the obtained results (Table 3) did not confirm those expectations. Impact strength remained at the level of the sole HIPS/$Mg(OH)_2$ mixture without any modifiers [8].

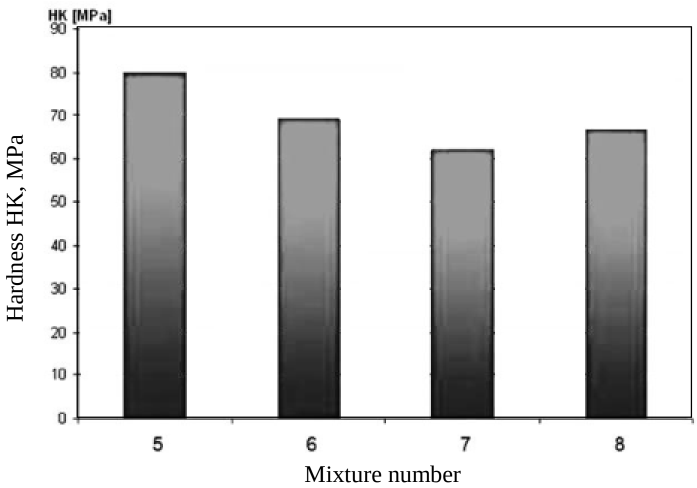

Fig. 1. Hardness of the mixture modified with SEBS
set 5-55% $Mg(OH)_2$, 30% HIPS, 15% SEBS; set 6-55% $Mg(OH)_2$, 40% HIPS, 5% SEBS; set 7-55% $Mg(OH)_2$, 31% HIPS, 14% SEBS ; set 8-55% $Mg(OH)_2$, 22,5% HIPS, 22,5% SEBS

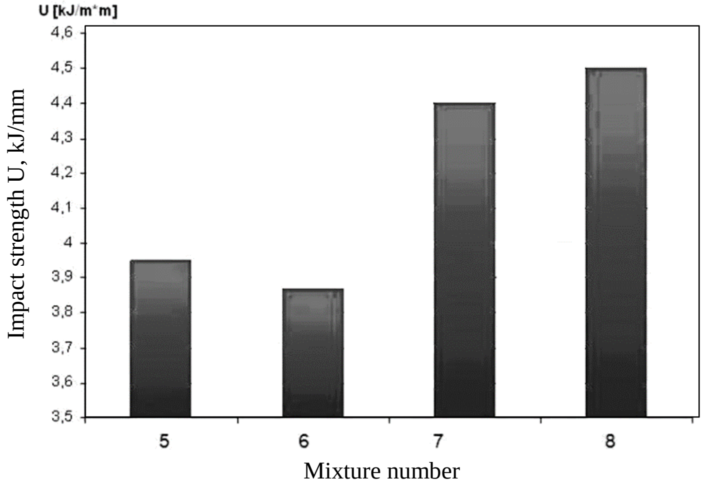

Fig. 2. Impact strength of the mixture modified with SEBS
set 5-55% $Mg(OH)_2$, 30% HIPS, 15% SEBS; set 6-55% $Mg(OH)_2$, 40% HIPS, 5% SEBS; set 7-55% $Mg(OH)_2$, 31% HIPS, 14% SEBS; set 8-55% $Mg(OH)_2$, 22,5% HIPS, 22,5% SEBS

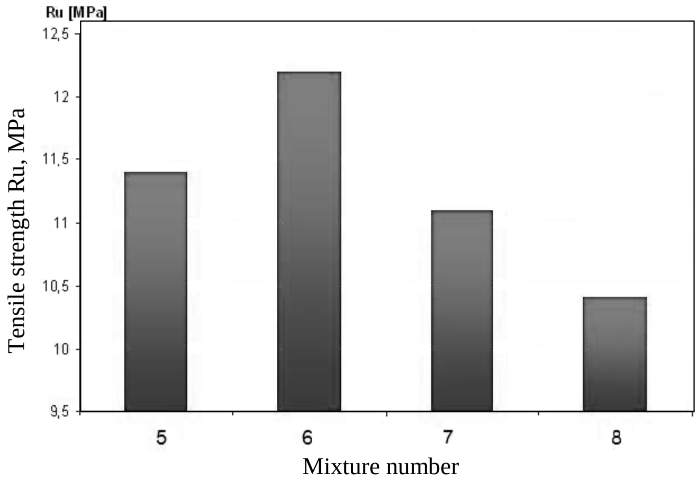

Fig. 3. Tensile strength for the mixture modified with SEBS
set 5-55% $Mg(OH)_2$, 30% HIPS, 15% SEBS; set 6-55% $Mg(OH)_2$, 40% HIPS, 5% SEBS; set 7-55% $Mg(OH)_2$, 31% HIPS, 14% SEBS; set 8-55% $Mg(OH)_2$, 22,5% HIPS, 22,5% SEBS

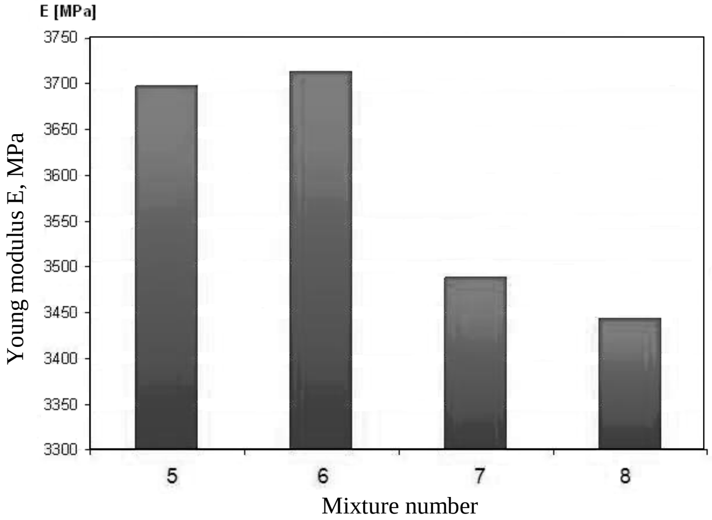

Fig. 4. Young modulus for the mixture modified with SEBS
set 5-55% $Mg(OH)_2$, 30% HIPS, 15% SEBS; set 6-55% $Mg(OH)_2$, 40% HIPS, 5% SEBS; set 7-55% $Mg(OH)_2$, 31% HIPS, 14% SEBS; set 8-55% $Mg(OH)_2$, 22,5% HIPS, 22,5% SEBS

As for the flame properties, all parameters remained at the satisfying level (Table 4).

Table 4. Flame properties of the non-flammable mixture modified with styrene-ethylene-butylene-styrene (SEBS)

Set	Filler Content, %			Flame parameters		
	$Mg(OH)_2$	HIPS	SEBS	Oxygen Index, %	Exposure *lxs*	Illumination intensity *lx*
5	55,0	30,0	15	25,50	20613,00	62,90
6	55,0	40,0	5	28,50	21405,00	79,30
7	55,0	31,0	14	28,50	21969,00	81,50
8	55,0	22,5	22,5	28,50	21749,00	80,00

In comparison to the results obtained in paper [4], the smoke emission was definitively lower (parameters presented in Figs. 5, 6). It is due to the fact that the SEBS itself emits less smoke than SBS. Oxygen index kept slightly above 28 except for set 5 where it dropped to as low as 25.5 (Fig. 7).

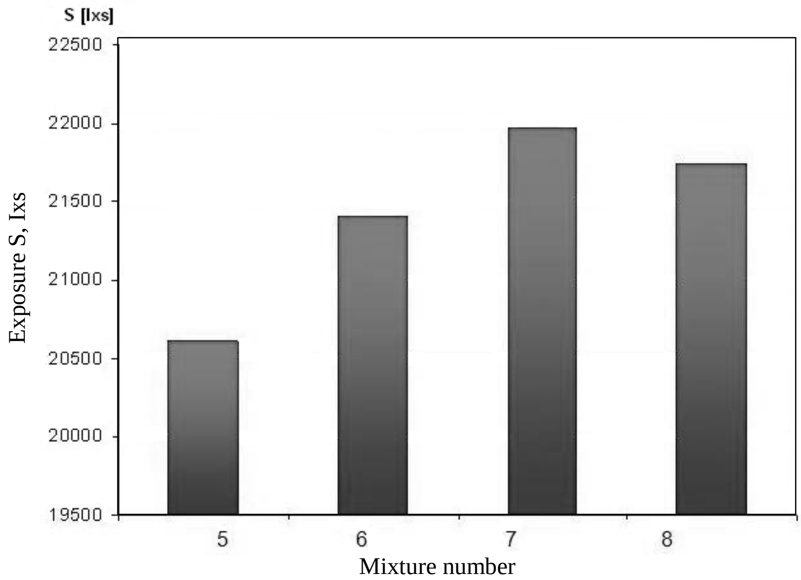

Fig. 5. Exposure S for the mixture modified with SEBS
set 5-55% $Mg(OH)_2$, 30% HIPS, 15% SEBS; set 6-55% $Mg(OH)_2$, 40% HIPS, 5% SEBS;
set 7-55% $Mg(OH)_2$, 31% HIPS, 14% SEBS; set 8-55% $Mg(OH)_2$, 22,5% HIPS, 22,5% SEBS

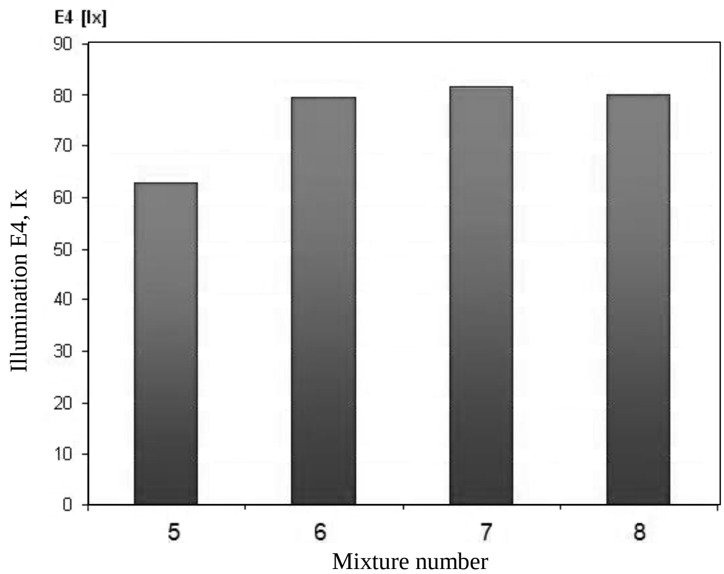

Fig. 6. Illumination E4 for the mixture modified with SEBS
set 5-55% $Mg(OH)_2$, 30% HIPS, 15% SEBS; set 6-55% $Mg(OH)_2$, 40% HIPS, 5% SEBS; set 7-55% $Mg(OH)_2$, 31% HIPS, 14% SEBS; set 8-55% $Mg(OH)_2$, 22,5% HIPS, 22,5% SEBS

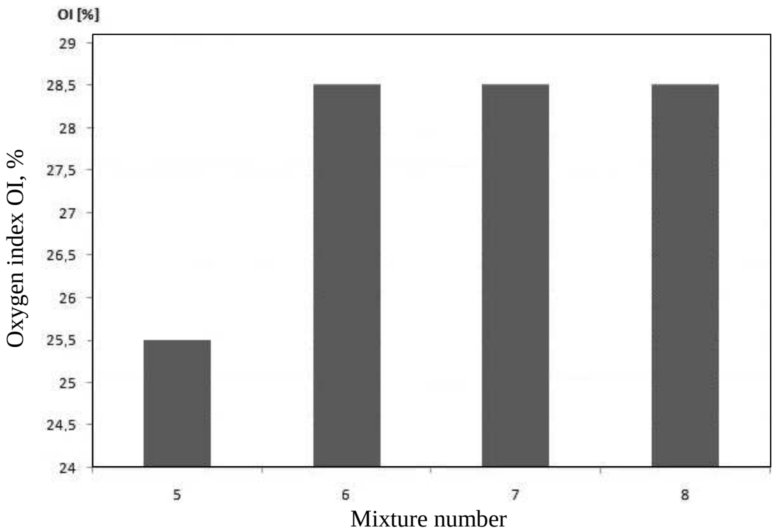

Fig. 7. Oxygen index for the mixture modified with SEBS
set 5-55% $Mg(OH)_2$, 30% HIPS, 15% SEBS; set 6-55% $Mg(OH)_2$, 40% HIPS, 5% SEBS;
set 7-55% $Mg(OH)_2$, 31% HIPS, 14% SEBS; set 8-55% $Mg(OH)_2$, 22,5% HIPS, 22,5% SEBS

The obtained results (Tables 3 and 4), show only a slight improvement in impact strength with the value of oxygen index oscillating around the limit of 28%. This led to further attempts to introduce one more additive – the previously used SBS [10].

The content of the mixture was as follows:

set 9-55% $Mg(OH)_2$, 23% HIPS, 11% SBS, 11% SEBS

In Tables 5 and 6, respectively, mechanical and flame properties are presented

Table 5. Mechanical properties for the mixture containing both SBS and SEBS

Set	**Filler content, %**				**Mechanical properties**			
	$Mg(OH)_2$	**HIPS**	**SBS**	**SEBS**	**Hardness $HK_{5,30}$** MPa	**Impact Strenght** KJ/m^2	**Tensile Strength** MPa	**Young Moduls** MPa
9	55,0	23,0	11,0	11	62,30	5,0	12,60	3761,00

Table 6. Flame properties for the mixture containing both SBS and SEBS

Set	**Filler content, %**				**Flame properties**		
	$Mg(OH)_2$	**HIPS**	**SBS**	**SEBS**	**Oxygen Index** %	**Exposure** lxs	**Illumination intensity** lx
9	55,0	23,0	11,0	11	26,50	20352,00	67,40

The purpose of testing this mixture was to check whether the SBS admixture would improve mechanical properties. Comparison of Tables 3 and 5 confirms these expectations. All mechanical parameters except hardness increased.

As for the flame parameters (compare Tables 4 and 6) the smoke emission was significantly lower. The oxygen index, however, dropped to the level 26.5% which resulted in the rejection of the material.

To sum up the results of these series of tests it is worthwhile to notice that SEBS did not essentially improve mechanical properties of the mixture in spite of having higher mechanical strength than SBS.

The smoke emission was reduced, the oxygen index, however, oscillated close to the value of 28.5% which is hardly acceptable.

In the case of set 9 where two thermoplastic elastomers were introduced (SBS plus SEBS), only impact strength rose slightly while oxygen index dropped to 26.5%.

Finally, it can be concluded that the best results were obtained in the cases where only SBS was used as the modifier of impact strength.

5. Conclusions

- Application of halogen flame retardant as an admixture to the basic mineral flame retardant gave no positive results in any aspect. Neither mechanical nor flame properties were improved, thus this path of research was abandoned.
- The SEBS elastomer mainly reduced smoke emission while oxygen index remained close to the lowest permissible limit.
- Application of both SEBS and SBS elastomers brought about little rise of mechanical parameters while oxygen index dropped to 26.5%
- The final conclusion of material selection is that the optimum non-flammable mixture would consist of three components: HIPS, $Mg(OH)_2$ and SBS.

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