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Rubber flame retardants based on organophosphorus compounds

In the work presented oxyethylidenediphosphonic acid and its ammonium salt were proposed as rubber flame retardants and rubber formulations were elaborated. The effect of the flame retardant additives on the mechanical properties of rubber was studied, and the degree of fire protection was determined. It was shown that the rubber with the addition of oxyethylidenediphosphonic acid had a higher degree of fire resistance compared to the rubber with oxyethylidenediphosphonic acid ammonium salt.

Key words: flame retardants, oxyethylidenediphosphonic acid, trichlorethylphosphate, oxyethylidenediphosphonic acid triammonium salt, vulcanization and scorching.

The use of flame retardants in order to reduce the flammability of rubber has long been known and effectively used these days. It was given the interpretation of the mechanism of action of individual substances and synergistic effect of combinations of various substances such as a mixture of antimony trioxide and chlorinated paraffin, or a combination of phosphates and borates, and hydroxides of magnesium and aluminum. However, the final decision on the effectiveness of certain flame retardants in each case can be made after the experiment. A direct transfer of data is not possible because of the large variety of rubber grades, rubber compounding ingredients and rubber mixtures formulations.

The purpose of this study is to search for effective flame retardants for rubbers which are used as inflammable rubberized conveyor belts as well as studying the impact of the proposed fire-retardant additives on the fire and heat resistance and other physical and mechanical properties.

In this work oxyethylidenediphosphonic acid and its ammonium salt were proposed as flame retardants for rubbers and a number of rubber formulations with the proposed retardants included were elaborated. The effect of these flame retardants on the mechanical properties of rubbers as well as the degree of their fire protection was determined.

In order to implement certain formulations in the production it is necessary that the resulting rubbers comply with all regulations and possess improved physical and mechanical properties; they should be economically viable as well [1, 2].

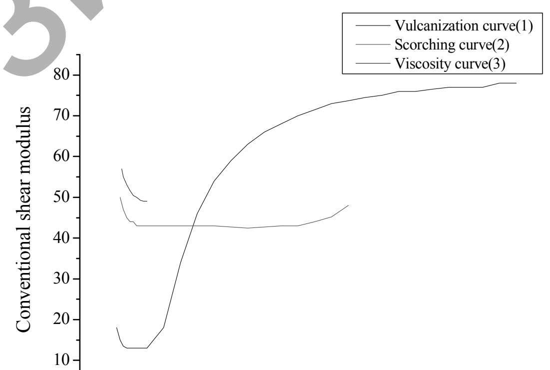
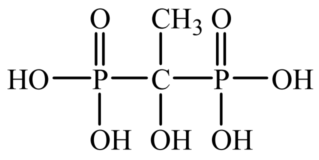


Figure 1. Kinetic curves of vulcanization and scorching, viscosity curve of standard rubber of TG grade

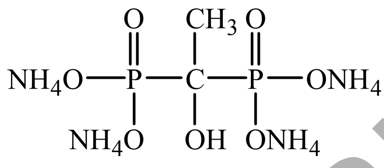
According to the vulcanization curve (Fig. 1) vulcanization induction period is 7 minutes, the optimum of vulcanization is 30 minutes, scorching time is 35 minutes on the basis of the scorching process curve and the viscosity is 49 Muni units.

Evaluation of flammability by burning rate of protected polyurethane foam shows that the addition of even 3–5 parts by weight of oxyethylidenediphosphonic acid (OEDFA) results in combustion stability decreasing by 3–3.5 times while traditional trichlorethylphosphate slows burning twice at 20 % filling [3]. However polyurethane degradation process accelerates in the presence of OEDFA, but it is shifted to a higher temperature region, thereby increasing the thermal stability as compared with trichlorethylphosphate. The reason for the effectiveness of OEDFA as a flame retardant is the formation of char residue that protects undecomposed polymers in the event of fire. OEDFA and its amine salts in combination with boric acid determine fireproof of rigid polyurethane foams [4].

OEDFA (I) and its triammonium salt (II) were selected as test objects due to the availability of these substances produced on an industrial scale, in particular the use of OEDFA is generally known as a chelator which is widely used in water treatment systems.



(I)



(II)

OEDFA triammonium salt attracts our attention because it contains a nitrogen atom in addition to the content of two phosphorus atoms in the molecule, being a potential nitrogen-and phosphorus-containing flame retardant. The presence of nitrogen-containing compounds in phosphorus-containing polymers facilitates the formation of polyphosphoric acid which is a dehydrated phosphorylating agent and a catalyst of coking process. Also, nitrogen, phosphorous-containing mixtures or compounds formed during their degradation decompose to release water and carbon with the possible formation of volatile nitrogen compounds to inhibit the combustion. The probability of forming of protective films of heat-resistant phosphorus and nitrogen compounds on the material surface is not excluded [5].

OEDFA triammonium salt crystalline hydrate was used as a target for the formulation number 1 wherein OEDFA was introduced into the rubber blend as the sole flame retardant (33 parts by weight). Samples of rubber produced by the recipe No.1 failed the fire test. After the removal of fire the samples did not cease to burn until complete destruction.

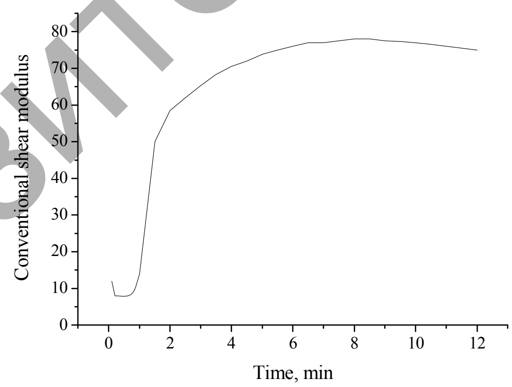


Figure 2. The kinetic curve of vulcanization process
for rubber produced by the formulation number 1

The vulcanization induction period decreases compared to the standard rubber and it is equal to 4 minutes (Fig. 2), the optimum of vulcanization is equal to 22 minutes. Then samples of rubber based on the formulation number 2 which contained a mixture of triple flame retardants, namely, chloroparaffin-70 (CP-70) — 15 parts by weight, antimony trioxide — 5 parts by weight and 10 pbw of ammonium salts of OEDFA passed the fire tests. Flame decay time was recorded for each sample (6 samples): 2.8 s, 3.6 s, 3.6 s, 2.6 s, 2.2 s, 2.4 s (17.2 s in total; 3.6 s is max). The norm for a shaft rubber of TG grade is 18–45 s, thus yielding rubber has acceptable fire-resistant characteristics. There is a slight deviation from the norm by conventional tensile strength, and the salt odds badly in the rubber mixture, which is already quite a significant disadvantage. Also the vulcanization induction period and the optimum decreases that means an increase in the flow of various adverse reactions which affects many properties of rubber, especially conventional tensile strength. According to the curve of the vulcanization induction period is equal to 7 minutes, the optimum of vulcanization is 25 minutes, the process of scorching is 34 minutes, and the viscosity is 40 Muni units (Fig. 3, 4).

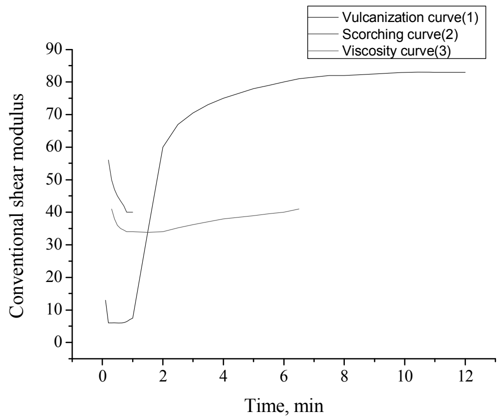


Figure 3. Kinetic curves of vulcanization process, scorching process and viscosity of rubber composition according to the formulation number 2

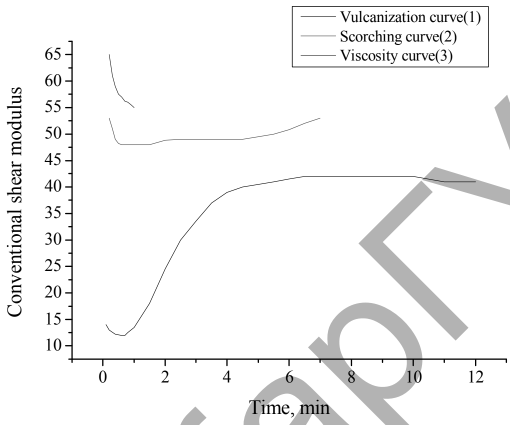


Figure 4. Kinetic curves of vulcanization process, scorching process and viscosity of rubber composition according to the formulation number 3

A fire test was carried out on samples of rubber containing flame retardants, comprising OEDFA, as the same parts by weight as OEDFA ammonium salt in the formulation number 2 (10 pbw) and 15 pbw of CP-70, 8 pbw of antimony trioxide. Time of flame quenching is measured: 1.6 s, 1.6 s, 1.2 s, 1.6 s, 1.6 s, 1.4 s (9 s in total; 1.6 s is max.).

Rubber with the addition of OEDFA has a great degree of fire protection. The improvement in flame retardancy compared to the ammonium salt can be attributed to the fact that acid is well dispersed in the mixture. However, the addition of OEDFA into the rubber composition has a very negative impact on some physical and mechanical properties; namely, the conditional strength in tension of rubber samples was significantly lower than normal.

According to the vulcanization curve the vulcanization induction period lasts 5.5 minutes and the vulcanization optimum is achieved within 20.5 minutes. The scorching process time is 35 minutes and the viscosity is 55 Muni units.

Physical and mechanical properties of the test for fire resistance of rubbers are presented in Table 1. Characteristics of the vulcanization process of the studied rubbers are presented in Table 2.

Table 1

Physical and mechanical properties of the test for fire resistance of rubbers

Formulation	Tensile strength, MPa	Elongation at break, %	Volume loss by abrasion, mm	Hardness on Shore units A	Combustion (ring)
Rate	≥14,7	≥350	≤200	55–70	15–45
Series	16,3	400	112	72	12,2–2,2
1	13,5	390	105	66	>>45
2	11,7	320	96	69	17,2–1,6
3	10,9	570	137	55	9,0–1,6

Table 2

Characteristics of the vulcanization process of the studied rubbers

Formulation	Induction period, min	Optimum, min	Time of scorching, min	Viscosity, Muni units
TG Series	7	30	35	49
1	4,5	21	–	–
2	7	25	34	40
3	5,5	20,5	35	55

Experimental part

Synthesis of ammonium salt of oxyethylidenediphosphonic acid (OEDFA)

70 g of OEDFA was dissolved in 100 mL of concentrated aqueous ammonia (28 %) in a 250 mL flask with a reflux. After dissolving the solution was boiled for 1 hour. The solution was cooled and the precipitate was filtered off. The product weight is 62.530 g. The yield is 73 %.

Physical and mechanical methods of testing of rubber samples

State Standard 270–75 «Rubber. The method of determining the elastic and strength properties at tensile» 23509–79 «Rubber. The method for the determination of abrasion resistance when sliding on renewable surface». The standard is widely used in assessing the quality of rubbers.

State Standard 263–75 «Rubber. Determination of hardness on Shore A. «The kinetics of vulcanization by rheometer «Monsanto» at temperatures 151.120 and 100 ºC according to State Standard 10722–76.

Research on fire protection of rubber samples of different formulations was carried out according to State Standard 12.1.044–89. Rubber belts are considered to have passed the test if the decay time of the samples does not exceed the standard values and their re-ignition does not occur when blowing.

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Фосфорорганикалық қосылыстар негізінде резеңкелер үшін жанудың тежеушілері

Мақалада алғаш рет оксиэтилидендифосфон қышқылы және оның аммонийлық тұзы резеңкелер үшін антипирендер ретінде ұсынылған және резеңкелер рецептураларының қатары өңделген. Зерттелген оттан қорғаушы қоспалардың резеңкелердің механикалық қасиеттеріне әсері, сонымен бірге олардың оттан қорғау деңгейі анықталған. Оксиэтилидендифосфон қышқылы қосылған резеңке құрамында аммонийлық тұзы бар резеңкелермен салыстырғанда жоғары оттан қорғау деңгейге ие екені көрсетілген.

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Замедлители горения для резин на основе фосфорорганических соединений

В статье впервые были предложены оксиэтилидендифосфоновая кислота и ее аммонийная соль в качестве антипиренов для резин и разработаны рецептуры резин. Изучено влияние исследуемых огнезащитных добавок на механические свойства резин, а также была определена степень их огнезащиты. Авторами показано, что резина с добавлением оксиэтилидендифосфоновой кислоты обладает высокой степенью огнезащиты в сравнении с аммонийной солью.

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