UDC 678(075.8)

L.K.Salkeyeva[1], G.T.Khassenova[1], Gerd-Volker Röschenthaler[2], Ye.K.Tayshibekova[1], Ye.V.Minayeva[1], A.A.Zhortarova[1], L.M.Sugralina[1], Ye.T.Sagatov[1], A.K.Salkeyeva[3]

[1]Ye.A.Buketov Karaganda State University;
[2]Jacobs University, Bremen, Germany;
[3]Karaganda State Technical University
(E-mail: lsalkeeva@mail.ru)

Heterocyclic flame retardants for rubber based on glycoluril and its derivatives

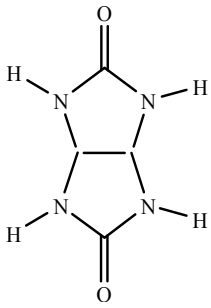
This article was first proposed to glycoluril and its derivatives as flame retardants for rubbers. The effect of flame retardants on mechanical properties of rubbers was studied. The degree of fire protection was determined. It was shown that the addition of rubber to tetra-N-methylolglycoluril with a synergistic blend of flame retardants had an excellent degree of fire protection in comparison with a series of fire resistant rubbers.

Key words: flame retardants, glycoluril, tetra-N-chloroglycoluril, tetra-N-methylolglycoluril, vulcanization and scorching.

Modern technological progress is impossible without extensive use of polymeric materials in various industries. Significant deterrent to the introduction of a variety of polymeric materials is their fire danger caused by flammability. At present time, the basic method of effective deceleration of combustion processes is the use of special additives such as flame retardants. Search for new additives that are highly effective at flame retardant action with absence of toxicity and adverse effect on the properties of the material, is a very urgent task [1].

Currently, urea derivatives are the most widespread among the nitrogen-containing heterocyclic flame retardants [2]. These compounds slow down combustion forming a voluminous polymer protective layer, thereby insulating the material from the heat source or heat. Such property can be further improved by adding substances with a synergistic action [3].

Bicyclic bisureas which include glycoluril and its derivatives attract the attention of chemists due to their use in pharmacology and various industries.



2,4,6,8-Tetraazabicyclo[3.3.0.]octane-3,7-dione (glycoluril) and its derivatives were chosen as the objects of the study to be tested as heterocyclic flame retardants. Rubbers based on synthetic isoprene rubber and synthetic vinyl rubber used as samples for research on fire resistance.

Because of the large variety of grades of rubber and rubber formulations direct transfer of data to a determined rubber compounding is not possible and the final decision on the effectiveness of certain flame retardants in each case is possible after the experiment [4].

The studied rubber composition consisted of the following components: rubber, zinc white, carbon black grade P-324, sulfur, sulfenamide C, magnesium oxide, zinc stearate, naphthame-2, diaphene, N-nitrosodiphenylamine, chloroparaffin-70, antimony trioxide, zinc borate, aluminum hydroxide.

As a reference, in this work, we used an extinguishant formulation which consists of 41 parts by weight of chloroparaffin-70 (CP-70), 10 parts by weight of antimony trioxide and 20 parts by weight of zinc borate and 20 parts by weight of aluminum hydroxide.

The total burning time of 6 samples of reference fire resistant rubber (rings) is 1.0 s (0.6 s-max) (Table 1). According to the curve of vulcanization the induction period of vulcanization is 9 minutes and the optimum of curing is 38 minutes. Refering to the scorch curve the scorch process time is more than 40 minutes, and a viscosity is in the range of 57 Mooney units (Fig. 1, Table 2).

Manufacture of the studied rubber compounds was carried out on rollers. Vulcanization of the samples was carried out in press.

In the rubber formulation # 1 it was used the synergistic mixture of flame retardants which includes 5 parts by weight of glycoluril together with 41 parts by weight of CP-70, 10 parts by weight of antimony tri-

oxide and 20 parts by weight of zinc borate and 20 parts by weight of aluminum hydroxide. These weight ratios of the studied flame retardant and inhibitors-synergists will be used in further formulations.

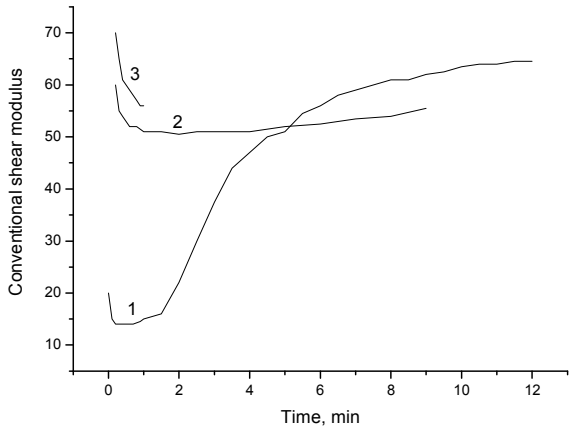


Figure 1. Kinetic curves of vulcanization and scorching, a viscosity curve of standard rubber of TG grade

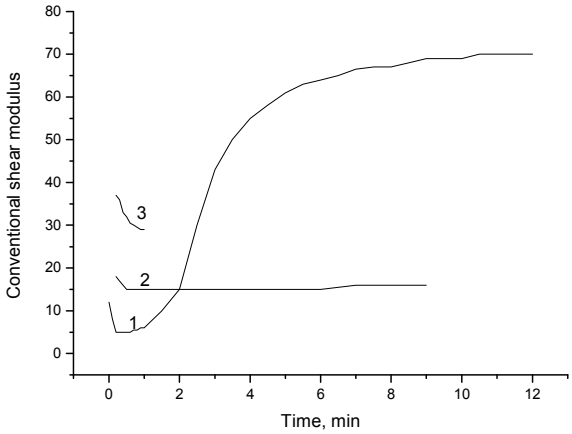


Figure 2. Kinetic curves of vulcanization (1), scorching of the rubber composition (2) and the viscosity (3) established according to the formulation #1

As a result, the total burning time for the 6 samples was 1.0; 1,0; 0.8; 0.8; 1.0 — 5.6 s (1.0 s-max.) overall (Table 1). It should be noted the positive impact of the additive on the stress-strain tensile properties, but there is a slight increase in the volume loss by abrasion (Fig. 2, Table 3).

Table 1

The results of the fire tests of the studied rubber samples

Formulation	Combustion (ring), s
Rate	18–5 max
FR Series	1,0–0,6 max
№ 1	5,6–1,0 max
№ 2	4,4–1,0 max
№ 3	1,0–0,4 max

Table 2

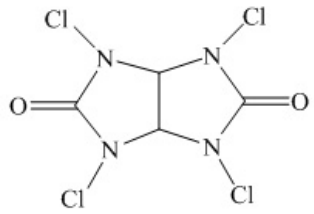
Characteristics of the vulcanization process of the studied rubbers

Formulation	Induction period, min	Optimum, min	Time of scorching, min	Viscosity, Mooney units
FR Series	9	38	>40	57
№ 1	8	31	>40	29
№ 2	7	42	30	27
№ 3	9	35	>40	29

Table 3

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
Rate	≥14,7	≥350	≤200	55–70
Series	13,5	490	199	71
№ 1	13,7	540	243	62
№ 2	13.5	570	263	61
№ 3	11,5	450	230	65



Halogenated triazine and geptazine derivatives are promising flame retardants to reduce the flammability of heat-resistant rubbers based on ethylene-propylene rubber. In this work tetrachloroglycoluril was proposed as potential nitrogen-, halogen-containing flame retardant and was inducted as 5 parts by weight into the formulation #2.

Fixed fire extinguishing time is 1.0 s, 0.6 s, 0.8 s, 1.0 s, 0.6 s, 0.4 s,-4.4 s (1.0 s-max.) overall (Table 1). There is a slight deviation from the norm for conventional tensile strength (Table 3).

According to the graph (Fig. 3), which shows the kinetic curves of vulcanization, the vulcanization optimum value is 42 minutes, the scorch time is 30 minutes, the induction period of vulcanization is 7 minutes. Based on the optimum value the reducing of the vulcanization rate is proposed.

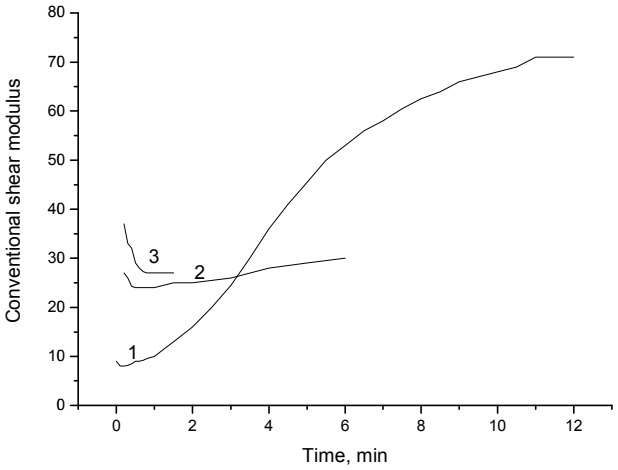
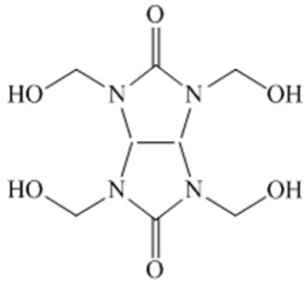


Figure 3. Vulcanization kinetics curves (1), the scorching of the rubber composition (2) and the viscosity (3) established according to the formulation #2

Being a glycoluril derivative, tetra-N-methylolglycoluril was proposed as a potential flame retardant Currently, this compound is preferably used as an effective stabilizer for natural or synthetic polymer products.

Possibility of using 2,4,6,8,-tetrametilol-2,4,6,8,-tetraazabicyclo[3.3.0.]octane-3,7-dione (tetramethylolglycoluril) as a flame retardant additive is due to several reasons. From the literature it is known the use of glycoluril-formaldehyde resins as flame retardants in the manufacture of polyurethanes. It should be noted that the structure of tetramethylolglycoluril contains hydroxyl groups which makes it similar to the polyols which are used as flame retardant additives capable of forming a protective intumescent coating on the surface of polymeric materials.



During the test tetra-N-methylolglycoluril was added to the rubber composition in 5 parts by weight together with 41 parts by weight of CP-70, 10 parts by weight of antimony trioxide and 20 parts by weight of zinc borate and 20 parts by weight of aluminum hydroxide. Fixed fire extinguishing time is: 0.0 s; 0.2 s; 0.0 s; 0.4 s; 0.4 s; 0.0s -1s (0.4 s-max.) overall (Table 1). Rubber with the addition of tetramethylolglycoluril has an excellent degree of fire protection and it is virtually non-combustible. However, this additive is not well diverges in the rubber composition mixture which is a significant disadvantage, as there is a slight deviation from the norm for conventional tensile strength (Table 3).

According to the graph (Fig. 4), which shows the kinetic curves of vulcanization, vulcanization optimum value is 35 minutes, the scorch time exceeds 40 minutes, the induction period of vulcanization is 9 minutes. Based on the vulcanization parameters it can be found the sufficient duration of the induction period during which a plastic condition persists without scorching.

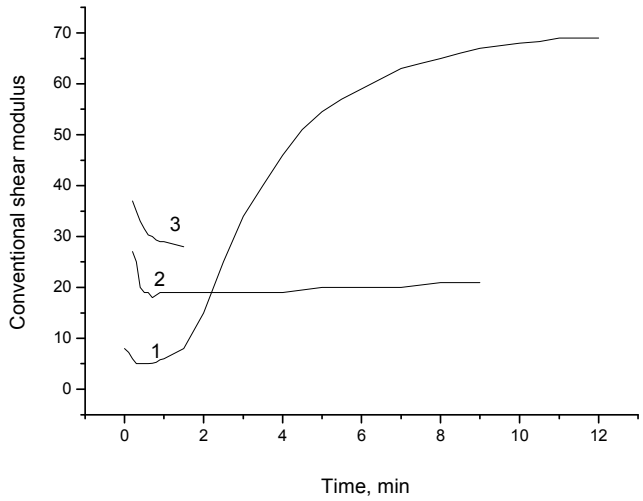


Figure 4. Kinetic curves vulcanization (1) scorching of the rubber composition (2) and the viscosity (3) established according to the formulation #3

Synergistic mixture of flame retardants which included antimony trioxide, chloroparaffin-70, aluminum hydroxide and zinc borate, attached to synthetic rubber isoprene and synthetic vinyl rubber, makes the rubber samples inflammable. Rubbers containing glycoluril and tetrachlorglycoluril showed relatively lower degree of fire resistance. However, it is known that some glycoluril derivatives are capable to retard the burning of chemical fibers, i.e. a negative result in the application of these synergistic mixtures for rubber can not be indicative of the absence of flame-retardant properties. It should be noted a positive impact of glycoluril on the stress-strain properties of rubbers. Introduction of tetra-N-methylolglycoluril resulted in higher degree of fire resistance even in comparison with the reference rubber which is virtually nonflammable. However, this additive disperses in the rubber mixture not well enough.

According to the conclusive data, the bicyclic bisureas derivatives in general have demonstrated satisfactory results regarding physical and mechanical properties of rubber as a whole. Noteworthy is the absence of negative effects on curing parameters. Rubber with the addition of tetra-N-methylolglycoluril has the best fire resistance among the tested rubber samples based on SIR-3 and SVR.

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.

References

1 *Халтуринский Н.А., Рудакова Т.А.* Физические аспекты горения полимеров и механизм действия ингибиторов // Химическая физика. — 2008. — Т. 27, № 6. — С. 71–82.

2 *Day A.I., Arnold A.P., Blanch R.J.* // B. J. Org. Chem. — 2001. — № 66. — P. 8094.

3 *Zaikov G.E.* Low Flammability Polymeric Materials // Polymer News. — July, 2005. — Vol. 30, № 7, Plinbu. — P. 216.

4 *Дик Дж.С.* Технология резины: Рецептуростроение и испытания / Под ред. В.А.Шершнева. — СПб.: НОТ, 2010. — 620 с.