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FLAMMABILITY OF BUTADIENE–ACRYLONITRILE RUBBERS

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Abstract

The paper discusses the test results of butadiene–acrylonitrile rubber, Perbunan NT 1845 and Perbunan NT 3945, flammability and properties that characterise these elastomers under fire conditions. The flammability was tested by means of oxygen index and thermovision methods. The thorough testing of flammability performed by means of a cone calorimeter made it possible to assess the behaviour of these polymers under fire conditions. The following properties of the tested copolymers were taken into account in this assessment: ignitability, heat release during combustion, smoke-forming capability and toxicity of the gaseous products of thermal decomposition and combustion. It has been found that the increase in the acrylonitrile unit content in the copolymer decreases its flammability and the relative toxic fire hazard, but clearly increases the smoke-forming capability and so the specific extinction area.

The interpretation of test results of the elastomers under investigation takes into consideration their thermal stability assessed on the basis of differential thermal analysis, thermogravimetry and other complementary methods.

Keywords: elastomer, flammability, flame temperature, thermal analysis, thermal stability

Introduction

The combustion process of solids can proceed according to different mechanisms depending on their chemical structures. A heterophasic mechanism occurs in the case of carbon combustion consisting in oxygen adsorption on carbon surface followed by a flameless oxidation. The combustion of polymers involves almost exclusively reactions between oxygen and the volatile products of thermal decomposition, thus it proceeds according to a homophasic mechanism.

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Most polymers, including the most common and manufactured on commercial scale, are inflammable materials. Some of them, e.g., polyolefines, cellulose and others, can be completely burnt even in an environment with a lower oxygen content than that of the atmospheric air. Therefore, the studies on polymer flammability and methods of its retardation, being of both considerable cognitive and practical importance, have been for years carried out in many national and international research centres [1–7].

The present paper shows a fragment of research performed at the Institute of Polymers, Technical University of Łódź, concerning the flammability of butadiene–acrylonitrile rubbers, commonly used in the rubber industry, and relevant fire hazard.

Experimental

The following butadiene–acrylonitrile rubbers, commonly known as nitrile rubbers, with various contents of acrylonitrile units in macromolecules were used in the studies: Perbunan NT 1845 (NBR 1845) and Perbunan NT 3945 (NBR 3945) of Bayer containing 18 and 39% of acrylonitrile units, respectively.

The flammability of these elastomers was determined by the method of oxygen index, using an apparatus of our own design, according to the standard PN-ISO 4589-2. The flammability in air was also tested, using the same specimens as in the case of oxygen index. The specimens placed vertically were ignited for 15 s by means of a burner supplied with a propane–butane mixture, and then the combustion time was measured [6, 7].

The flammability of the polymers under investigation was also determined by the method of cone calorimeter, using an apparatus of Atlas Electric Devices Company. This apparatus is suitable for the thorough testing of materials in respect of their fire characteristics. Elastomer specimens with dimensions 100×100±1 mm and thickness 2.0±0.5 mm were conditioned to a constant mass at a temperature of 20±2°C and *RH* 50±5% and tested in horizontal position according to ISO 5660 with a radiant heat flux density of 35 kW m^{-2}. During testing the following parameters are recorded: initial specimen mass, ignition time, specimen mass during testing, exhaust gas temperature and pressure, O_2, CO_2 and CO concentrations in tested exhaust gas, as well as extinction coefficient, final specimen mass and test length. The time to sustained ignition is that moment since the test start when the flame is sustained for at least 10 s.

The flame temperature during elastomer combustion was determined by means of thermovision. The thermal images of horizontally burning specimens were recorded at the emissivity coefficient e=0.62. This value was found by means of a therocouple, type K, TFN 1293 of EBRO with the measuring range from –200 to 1200°C and a thermovision camera Therma CAM PM 595 operating from 200 to 2000°C within the spectrum range from 7.5 to 13 μm with a built-in atmospheric filter with a cut-off wave of 7.5 μm. This is a commonly used method for the determination of emissivity coefficient of objects observed by thermovision.

Results and discussion

The combustion of most elastomers is accompanied by the formation of liquid decomposition products which flowing down along the tested specimen constitute an additional heat transfer medium and increase the contact with oxygen. These phenomena make flammability testing considerably difficult, but they are absent in the case of butadiene–acrylonitrile rubbers which tend to be thermally cross-linked and due to considerable intermolecular interactions form solid thermal decomposition products [8, 9]. We have found no agreement between the results of flammability and calculated on the basis of the empirical relationship shown by Johnson, which takes into account the heat of combustion that was even used to classify materials as flammable and non-flammable [10, 11]. Johnson's equation is however satisfied by few polymers as according to Hindersinn and Wagner [12] there is no relationship between flammability and the heat of combustion since under the conditions of flammability testing the combustion of a polymer is incomplete and departs from adiabatic conditions under oxygen atmosphere. The values of oxygen index, *OI*, allowing one to classify the examined polymers as flammable, do not indicate that one of them, namely NBR 39, is extinguished after 95 s (Table 1). Our previous tests showed that elastomers with considerably higher values of *OI* amounting to 0.370 owing to appropriately selected antipyrenes, were completely burnt in air [7]. The lower flammability of NBR 39 rubber in comparison with that of NBR 18 is associated with the higher content of acrylonitrile units in its macromolecules, which increases the activation energy of destruction, decreases the rate of this process and consequently decreases the formation rate of thermal decomposition products. This was shown by our test results obtained by means of thermal analysis (Table 2) [8] and cone calorimetry (Fig. 1). At the same time, the boundary layer of burning NBR 39 formed from the cross-linked, and more cyclised polymer than in the case of NBR 18, makes the mass and energy flow between specimen and flame difficult.

A significant effect on flammability is exerted by the products of thermal decomposition. The polymers under investigation contain in their composition also ni-

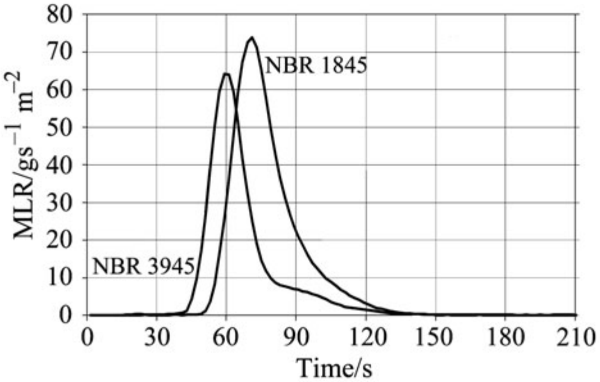

Fig. 1 The mass loss rate of butadiene–acrylonitrile rubbers determined by cone calorimeter

Table 1 The results of butadiene–acrylonitrile rubbers flammability investigations

Rubber	*OI*		Time of burning in air/s	H_c[2]/ MJ g^{-1}	Composition[3] of boundary layer/%	Composition[5] of carbon formed during burning/%
	determined	calculated[1]				
NBR 18	0.227	0.187	360	42.54	C=75.25; H=9.10 N=4.25; O=11.40	C=89.03; H=1.85 N=1.62; O=7.50
NBR 39	0.259	0.201	395[4]	39.61	C=77.46; H=8.39 N=8.60; O=5.55	C=91.47; H=1.42 N=2.11; O=5.00

[1] *OI* value calculated according to Johnson equation [10].

[2] Combustion heat determined by bomb calorimeter [9].

[3] The results of elementary analysis of boundary layer after 30 s of elastomer being under combustion in air. The boundary layer separated from the sample in depth $h\leq 1.0$ mm, after 3 h after its extinguishing. The results of elementary analysis of elastomers, in %:
NBR 18: C= 83.84; H=10.51; N=4.98; O=0.67
NBR 39: C=79.17; H=10.17; N=10.24; O=0.42
The elementary analysis were made in Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences, Łódź, Poland.

[4] Vertically located sample is extinguished in the air.

[5] The results of elementary analysis of carbon black formed during the flammability determination by the method of oxygen index.

trogen compounds which enter the flame and cause the combustion rate to decrease [1–7]. We have found that nitrogen compounds are also adsorbed on the surface of carbon black that is a basic component of the smoke being formed during polymer combustion (Table 1). The higher content of nitrogen compounds in the flame of burning NBR 39 rubber as compared to NBR 18 is also a significant cause of its lower flammability. This is confirmed by the thermovision tests. The flame temperature of NBR 18 is considerably higher than that of NBR 39 (Fig. 2).

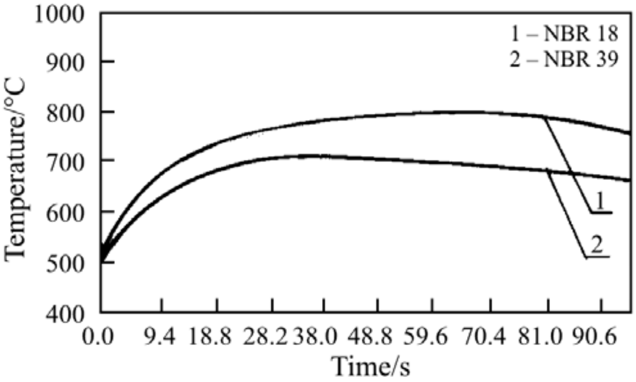

Fig. 2 Temperature distribution of the flame during combustion of butadiene–acrylonitrile rubbers

Our test results show that conduction, convection and radiation constitute a basic source of thermal energy that is indispensable to sustain the thermal decomposition of the examined butadiene–acrylonitrile copolymers. On the other hand, the strongly exothermic oxidising reactions in the surface layer, between the solid and gas phases, play in this case no significant role, specially in the case of NBR 39 (Table 1). The boundary layers of burning elastomers contain small quantities of oxygen amounting to 5.55 and 11.40%, respectively. From the literature review and previous studies performed at our Institute it follows that the content of oxygen in the boundary layer diffusing from the environment as a result of chemisorption processes may be considerably higher [7, 9, 13, 14].

The method of oxygen index is commonly used for testing polymer flammability. However, it should be clearly stressed that the value of *OI* can be used for a comparative assessment of flammability, but they constitute no basis for classification in respect of fire hazard. So far, there is no perfect method for testing material properties that determine a fire hazard. It is assumed that the basic material properties that characterise the behaviour of a polymer under fire conditions include: ignitability measured as the time to sustained ignition, total heat release, the smoke-forming capability and toxicity of the gaseous products of thermal decomposition and combustion. The first three parameters are given in Table 3. The smoke-forming capability is often measured as the specific extinction area (*SEA*). However fire hazard and toxicity we calculated from the results obtained with the cone calorimeter (Table 4). The fire hazard connected with the fire propagation rate, 1/*t* flashover or the inverse time to reach the effect of flashover was calculated according to Babrauskas [15].

Table 2 The results of thermal analysis of butadiene–acrylonitrile rubbers in air atmosphere

Elastomer	NBR 1845		NBR 3945	
Transition temperature/°C	180	315	190	330
Crosslink density/mol kg^{-1}	0.0614	0.1172	0.0069	0.0264
Thermal decomposition rate, (d*m*/d*t*)/mm	10		7	
Residue after thermal decomposition/%	8.2		14.4	
Activation energy of destruction, E_a/kJ mol^{-1}	149.5		162.0	

The relative toxic fire hazard (RTFH) of the elastomers under investigation was calculated on the basis of mass loss rate (MLR), time to sustained ignition (TTI) and exhaust gas yield. As the use of the cone calorimeter allows one to determine only the CO and CO_2 yields, the RTFH indexes found by us concern these gases. They were calculated from the formula presented by Babrauskas [15], taking into consideration $LC_{50}CO$ and $LC_{50}CO_2$ values from Polish Standard: PN-88/B-02855.

From the tests performed by means of the cone calorimeter it follows that the average maximum heat release, HRR_{max}, of NBR 18 is considerably higher than that of NBR 39 (Tab. 2). It should be stressed that during combustion of the tested rubbers the heat release is very high as compared to the commonly used polymers such as polyethylene or polypropylene for which this parameter amounts to 1830 and 1995 Kw/m^2 [19, 20]. Also the 1/t flashover assessed on the basis of the ignition time and HRR_{max} of both the tested elastomers is higher (Table 3) as compared with polyethylene and polypropylene whose corresponding values amount to 20.15 and 45.22, respectively [19, 20]. From the literature review it follows that 55 – 75% of fatal accidents during fires are caused by poisoning with combustion and decomposition products including smoke [16, 17]. Thus, the problem of toxic emissions becomes more and more important. The testing of the toxicity of thermal decomposition and com-

Table 3 The means values of parameters of butadiene–acrylonitrile rubbers determined by cone calorimeter

Parameter	Rubber	
	NBR 1845	NBR 3945
Time to sustained ignition/s	54.20	47.29
Average heat release rate/kW m^{-2}	1306.64	1015.26
Peak heat release rate/kW m^{-2}	3569.23	3115.28
Total heat release/MJ m^{-2}	99.71	67.27
Average effective heat of combustions/MJ/kg	50.05	47.14
Average mass loss rate/g s^{-1} m^{-2}	41.61	31.83
Average specific extinction area/m^2 kg^{-1}	720.90	797.18
Average CO yield	0.097	0.082
Average CO_2 yield	3.262	2.896

Table 4 The butadiene–acrylonitrile rubber properties describing their behaviour in the fire conditions

Parameter	Rubber	
	NBR 18	NBR 39
$1/t_{\text{flashover,}}$ fire hazard, kW m^{-2} s^{-1}	65.87	65.88
$RTHF_{CO/CO_2}$, relative toxic fire hazard	0.0326	0.0246

bustion products consists in quantitative chemical determination of specific yields of CO, CO_2, HCN, NO_2, HCl and SO_2 , which are then used to determine the toxicometric index [18]. The relative toxic fire hazard indexes, $RTFH_{CO/CO2}$, found by us, take into account, as mentioned above, only the emissions of CO and CO_2 . Considering the values of this index of the tested elastomers (Tab. 3), one should state that these polymers create a considerably higher hazard than polyethylene or polypropylene whose values of $RTFH_{CO/CO2}$ are significantly lower and amount to 0.0051 and 0.0138, respectively [19, 20]. Under fire conditions including nitrile rubbers, one should expect the emission of nitrogen compounds (Table 1) that are absent in the composition of products of thermal decomposition and combustion of hydrocarbon polymers, and so the extent of hazard in the case of the elestomers under investigation may be higher, which will be carefully assessed by us. Our studies continue to decrease the flammability of elastomers and the fire hazard involved through an appropriate selection of the composition of composites. An important part in this regard may be plaid by nanocomposites.

Conclusions

- In the assessment of elastomer flammability an important part is played by the results obtained by the methods of thermal analysis. The lower flammability of NBR 39 rubber as compared with that of NBR 18 results largely from the lower rate of its thermal decomposition due to its higher activation energy of destruction.
- The differences in the flammability of elastomers are affected by their thermal cross-linking capabilities. The cross-linking results in the formation of a stable insulating boundary layer that makes the mass and energy flow difficult. The polymer susceptibility to thermal cyclization plays also an important part.
- The flammability of elastomers can be assessed on the basis of the commonly used oxygen index as well as the measurements of the flame temperature. Thus, the method of thermovision plays a significant role.
- Conduction, convection and radiation constitute the basic source of thermal energy indispensable to sustain the thermal decomposition processes of the tested butadiene–acrylonitrile copolymers, while the exothermic oxidation reactions within the surface layer, between the solid and gaseous phases play no significant role, especially in the case of NBR 39.

- The assessed by the cone calorimetry parameters that characterise the behaviour of the tested butadiene–acrylonitrile copolymers under fire conditions have shown that they constitute a considerably greater hazard as compared to that of the commonly used polymers such as polyethylene or polypropylene.

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