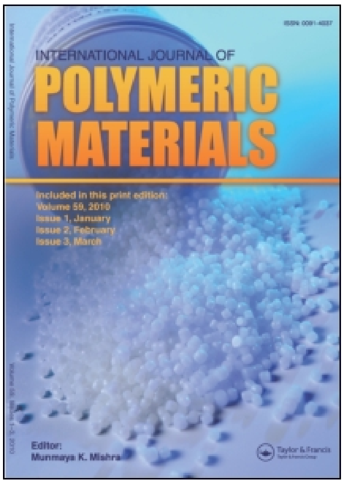

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The Combustion of Rigid Polyurethane Foams

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The Combustion of Rigid Polyurethane Foams

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The effect of the porous structure on the flammability characteristics of rigid polyurethane foams is studied. It is found that the velocity of the downward flame spread over the surface of foam slabs increases as the oxygen content into the ambient flow increases and the effective density of PU foams decreases.

The measurements of temperature profiles into the combustion wave made by Pt–PtRh thermocouples are used for the determination of the rate-controlling energy-transfer mechanisms.

KEYWORDS: Rigid polyurethane, foams, combustion, porous structures, flame spread, temperature profiles

Polyurethane foams are occupying the leading position among other cellular polymers. In rigid form PU foams are met in a range of different applications within buildings and transport. These cellular polymers are popular due to their simple technology of production, relatively low cost, high insulation properties and other positive qualities. However the common rigid PU foams may present serious fire hazard. The understanding of the fire behaviour of cellular polymers at the different situations is very important for the progress in the development of new fire safety materials, composites and constructions involving polymeric foams. There are a considerable number of the tests to study the flammability and fire hazard of cellular materials. Although there are the difficulties in relating the results of small-scale flammability test of cellular polymers to real fire behaviour, they continue to be of value for a number of investigational purposes.

The objective of this study as the first step is to determine experimentally characteristics of the downward laminar diffusion flame spread over PU foam slab by using LOI test apparatus. It was interesting to examine the effect of porous foam structure (apparent density) and also other factors on the flame spread velocity. The mechanism of heat transfer from the creeping flame to unburned combustible solid surface determines the flame spread one. Therefore, in order to elucidate this question temperature profiles near the leading edge of the flame have been examined in detail.

In the present work two types of PU foams were used:

1) foams based on GE-410 polyether polyol obtained by addition epichlorhydrin to glycerol and Rokopol T (propoxylated mixture of toluene diamines and triethanolamine)

2) foams based on Laprol-805 polyol (the product of polyoxypropylenation of ethylene glycol) and *N*-containing polyol-Lapromol 294 with an average functionality of 3.

The mixture of freon-11 and water was used as blowing agent. The foams were prepared according to the standard formulations given in Table I.

The apparent density of the samples obtained by a hand-mix technique was changed into the limits of 27–150 kg/m^3. The same properties of these PU foams are shown in Table II.

TABLE I

Formulations for rigid polyurethane foams

Ingredients	Part by weight
PU foams I	
Polyol GE-410	75
Polyol Rokopol T	25
Water	1.0
Silicone L 5340	1.0
Amine Catalyst	2.0
Polyisocyanate Desmodur 44V20	125
Freon 11	0–30
PU foams II	
Poluol Laprol 805 (TC-05-1679-74) Polyol Lapromol 294 (TC6-05-1681-74)	100
Polyisocyanate (TC6-02-727-78)	125
Dimethylethanolamine	2.0
Freon 11	0–30

TABLE II

The properties of rigid polyurethane foams

Property	PU foam I	PU foam II
Apparent density, kg/m^3	30	40
Compressive strength, kPa	240	197
Softening point, °C	141	—
Temperature of decomposition in air, °C:		
T_{begin}	210	210
$T_{10\%}$	257	260
Ignition temperature, °C[a]	—	360
Self-ignition temperature, °C	—	530
LOI, %	22.5	22.4
Burning rate, mm/s[b]	0.82	—
CT INdex[a]	5	4.8

[a] GOST 12.1.044-84.

[B] ASTM D 1692.

The more detailed information about the properties of the original ingredients and cellular products and also about the foams preparation technique may be found in the articles.[1,2]

According to Soviet standard GOST 12.1.044-84 the flammability test named by ceramic tube method is used for the rating of the materials flammability. CT index represents the ratio of the heat released as a result of polymer combustion to the heat required for the sample ignition. At the values of CT Index <1 polymeric material is classsified as hardly combustible. When $\text{CT} \geqslant 1$, material is combustible. The group of hardly flammable materials is characterized by the values of CT Index into the limits of 1–2.5. The PU foams studied are combustible. It was found that the effect of porosity (apparent density) of the cellular polymers on LOI and CT Index is insignificant. For instance when the PU foam-II density was changed from 40 to 140 kg/m^3 the LOI was equal to 22.4–23.5%. The mass burning rate at limiting combustion conditions was of 4.5×10^{-2} g/cm^2 s.

The flame spread over a polymer surface is a remarkably complex phenomena. The review of the experimental and theoretical investigations of the flame spread mechanisms was made by A. Fernandez–Pello.[3] Many factors affect the flame spread velocity (the oxygen content, temperature, sample orientation, the direction of the combustion wave and the air flow, size of sample, etc.). In present work it was shown that the flame spread velocity depends on cellular structure of PU (apparent density of foams). In general form the dependence is described by the empirical equation:

$$V_{fs} = K\rho^{-n}$$

where K and n are constants, $\rho = v_s\rho_s$, v_s-volume fraction of solid in foam, ρ_s-polymer density.

Table III demonstrates the experimental results, obtained for the flame spread over PU foams samples in the downward vertical and the horizontal directions.

It should be noted that the rate of flame spread along the free edges of the foam sample tested will always exceed the normal spread velocity. Therefore in the experiments with the measurement of the temperature profiles the flame spread along edges formed by the fuel has been avoided by means of the edges screening with aid of the liquid glass.

Table III shows that the flame spread velocity in horizontal direction is practically equal to the rate in downward vertical one. The "n" values in Eq. (1) almost approach to the theoretical one, $n = 1$. Thus low density PU foams can develop a high velocity of flame spread.

The considerable effect on the flame spread velocity over PU foams is found to have oxygen content into $(O_2 + N_2)$ oxydant flow (Table IV). This effect is increased when the apparent foam density is decreased.

The dependence of the flame spread velocity over PU foam having $\rho =$ 45 kg/m^3 on oxygen content is approximated by the equation:

$$V_{fs} = 1.89 \times 10^3 Y_{\text{ox}}^{4.2} \text{ mm/s}$$

The flame spread can be considered as successive ignition of pyrolysis gases

TABLE III

The effect of apparent density of PU foams on the downward, vertical and horizontal flame spread velocities

PU foams-I	ρ, kg/m^3	30.9	31.2	33.5	34.6	47.6	48	48.8	75	77.8
	↓ V_{fs}, mm/s	7.4	7.36	5.45	4.93	3.84	3.7	3.26	2.8	2.6
$Y_{O_2} = 0.265$	↓ without screen		$V_{fs} = 2.76 \times 10^2 \rho^{-1.1}$							
	↓ V_{fs}, mm/s with screen	—	5.0	—	2.44	—	—	2.0	—	1.33
PU foams-II	ρ, kg/m^3	30	45	55	59	64	67	85	135	145150
	↓ V_{fs}, mm/s without screen	14.9	12	9.4	6.8	7.0	6.5	5.35	5.45	4.2
			$V_{fs} = 1.22 \times 10^2 \rho^{-0.67}$							
$Y_{O_2} = 0.3$	→ V_{fs}, mm/s without screen	—	12	—	—	—	—	—	5.4	—
$Y_{O_2} = 0.235$	↓ V_{fs}, mm/s without screen	—	4.3	3.34	2.86	1.76	1.54	—	1.58	1.5
			$V_{fs} = 0.52 \times 10^2 \rho^{-0.75}$							

TABLE IV

The effect of oxygen content on the flame spread velocity over PU foams

PU foams I = 49 kg/m^3	Y_{O_2} vol. fraction	0.26	0.265	0.275	0.28	
	↓V_{fs}, mm/s	3.46	3.6	5.2	6.5	
	without screen	$V_{fs} = 3.7 \times 10^5 Y_{ox}^{8.5}$				
PU foams II = 70 kg/m^3	Y_{O_2} vol. fraction	0.25	0.257	0.26	0.28	0.30
	↓V_{fs}, mm/s	1.18	1.58	2.41	2.8	4.0
	without screen	$V_{fs} = 3.4 \times 10^4 Y_{ox}^{7.4}$				

formed as the result of preheating of porous surface layer of fuel to an ignition temperature by energy transferred from combustion zone to the fuel.[3] To measure the temperature histories of PU foam surface and gaseous phase near the flame leading edge the platinum–platinum 10% rhodium thermocouples with noncatalytic coating were used (bead diameter 0.1 mm). Micro-manipulator positioned thermocouples at 0.25 mm intervals normal to the vertical surface. The special marker was used for the determination of the moment of flame arrival to absolute distance scale. The temperature-time (distance) graphs were recorded by H115 oscillograph. Figure 1 shows some temperature profiles obtained for the steady downward flame spread along vertical slab of PU foam I having

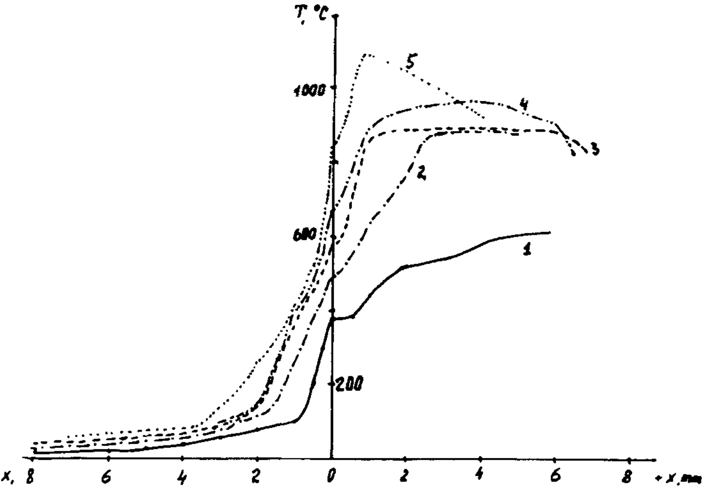

FIGURE 1 Temperature histories for downward spread of flame over PU foam. The position of bead, y, mm: 1—0; 2—0.75; 3—1.25; 4—1.5; 5—1.5 ($Y_{O_2} = 0.265$).

$\rho = 49\ \mathrm{kg/m^3}$. ($Y_{O_2} = 0.2$). The foam samples of the standard size of 1.2 × 1.25 × 15.0 cm exhibit the behaviour of a thermally thick material.

The thickness of the surface porous layer heated under the flame leading edge is equal to $\delta_{cy} = \sqrt{(a\delta_{cx}/Y_{fs})}$ where a is thermal diffusivity of PU foam, δ_{cx} is the distance of heat transfer ahead flame front.

At the conditions studied δ_{cy} is equal to 1.1 mm. The surface temperature is 375°C. The flame leading edge is disposed above the surface of PU foam at $y = 1.5$ mm. Maximum flame temperature is 1220–1370 K.

The temperature data were used to construct an energy balance for the condensed phase. For laminar flame spread over PU foam samples of small size the heat feedback from the flame to the unburned surface is used to raise the temperature of the fuel layer ($\dot{q}_h$) and to pyrolyze the fuel ($\dot{q}_{\mathrm{pyr}}$):

$$\dot{q}_s = \dot{q}_h + \dot{q}_{\mathrm{pyr}}$$

at $x < 0$, $\dot{q}_s \approx \dot{q}_h$ for steady process.

In the case considered the heat transfer mechanisms to unburned foam surface are probably gas-phase conduction, and solid-phase conduction through cellular surface layer with depth of δ_{cy}. From the data on V_{fs}, T, $\partial T/\partial x$ and $\partial T/\partial y$ the values of $\dot{q}_h$, $\dot{q}_{cs}$, $\dot{q}_g$ were calculated separately as functions of x.

The net flux of thermal entalpy is $\dot{q}_h = \delta_{cy}\rho V_{fs}c(T - T_0)$. The heat transferred by gas-phase is

$$\dot{q}_g = \lambda_g\left(\frac{\partial T}{\partial y}\right)_{x,y}, \qquad \dot{q}_{cs} = \delta_{cy}\lambda_s\left(\frac{\partial T}{\partial x}\right)_{x,0}$$

Table V lists average thermophysical properties for PU foams which we used for the calculation.

Figure 2 demonstrates a considerable fraction of heat transfer from the flame

TABLE V
Properties of PU foam

Property	PU foam-I	PU foam-II
Apparent density, kg/m^3	49	40
Porosity, %	96.1	96.6
Thermal conductivity, w/mK $\lambda_s = 2.85 \times 10^{-2} + 0.85 \times 10\,\rho^{-4}$	0.033	0.032
Thermal diffusivity, m^2/g $a \times 10^7 = 218/\rho + 0.3$	4.75	5.76
Heat capacity $c \times 10^{-3}$, J/kg · K $c = \lambda/a\rho$	1.42	1.39
Thermal inertia $\lambda\rho c \times 10^{-3}$ (w^2/m^2 K^2) s	2.3	1.78

by the conduction through porous layer near the leading flame edge (to 30–40% of the heat was transferred within 0.5 mm in the flame front.)

It is found that surface temperature increases to 405–410°C by increasing the oxygen content into air flow to 28%. It also increases the flame temperature and the flame spread velocity, but reduces the thickness of heated surface cellular layer.

Due to low thermal inertia of PU foam the heat transferred from flame to the unburned cellular body is accumulated into thin surface layer.

Thus in this small scale creeping flame spread over PU foam the heat transfer through gas phase (by conduction or convection) become dominant mechanism of the heat transfer from flame.

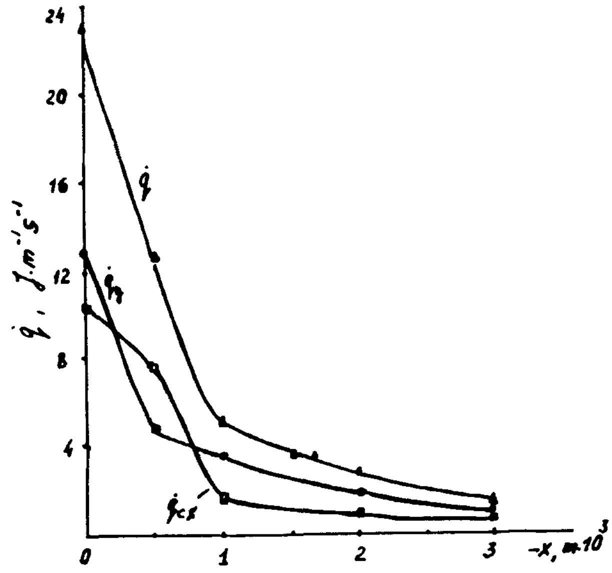

FIGURE 2 Heat feedback distribution ahead of flame front.

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