

Journal of Cellular Plastics

<http://cel.sagepub.com/>

Flexible Polyurethane Foam with the Flame-retardant Melamine

A. König, U. Fehrenbacher, T. Hirth and E. Kroke

Journal of Cellular Plastics 2008 44: 469

DOI: 10.1177/0021955X08095502

The online version of this article can be found at:

<http://cel.sagepub.com/content/44/6/469>

Published by:



<http://www.sagepublications.com>

Additional services and information for *Journal of Cellular Plastics* can be found at:

Email Alerts: <http://cel.sagepub.com/cgi/alerts>

Subscriptions: <http://cel.sagepub.com/subscriptions>

Reprints: <http://www.sagepub.com/journalsReprints.nav>

Permissions: <http://www.sagepub.com/journalsPermissions.nav>

Citations: <http://cel.sagepub.com/content/44/6/469.refs.html>

>> [Version of Record](#) - Nov 6, 2008

[What is This?](#)

Flexible Polyurethane Foam with the Flame-retardant Melamine

A. KÖNIG,* U. FEHRENBACHER AND T. HIRTH

Fraunhofer-Institut für Chemische Technologie, 76327 Pfinztal, Germany

E. KROKE

*Technische Universität Freiberg, Institut für
Anorganische Chemie, 09596 Freiberg, Germany*

ABSTRACT: Flexible polyurethane (PU) foams are widely used in many industrial applications, such as upholstered furniture and mattresses, automotive applications, etc. The chemical nature of the PU, the high air permeability, and the high inner surface area of the foam structure cause this material to be highly flammable. Consequently, the application of flame retardants to flexible PU foams is an important issue. The use of halogenated flame retardants is not considered optimal, in part due to the high emission level and the possible phase-out by the European Risk Assessment Body. Consequently, melamine as a nonhalogenated flame retardant is applied more and more frequently. However, little data is available regarding the application of melamine as an additive in flexible PU. This paper is concerned with the influence of melamine on the synthesis of the PU foam and the resulting material-specific properties. Especially, the increase of viscosity and the high heat capacity of melamine lead to a decrease in foaming growth and rising height with increasing melamine content. This is caused by the reduced drainage rate between the struts and the plateau borders in the foam-forming process. Here, the increase in viscosity follows the Dougherty–Krieger equation with the intrinsic viscosity of $k = 3.3$. The mechanical properties such as density and compression strength increase with increasing melamine content. Other properties like tensile strength and elongation decrease because of the embedding of the melamine in the PU matrix, which weakens the structure. The air permeation and number of cells also decreases because of the thickened struts caused by the reduced drainage rate in the foaming process. Furthermore, the reaction between the amino groups of melamine and the isocyanate of the PU formulation was investigated by FTIR.

*Author to whom correspondence should be addressed.

E-mail: alexander.koenig@ict.fhg.de

JOURNAL OF CELLULAR PLASTICS Volume 44 — November 2008

469

0021-955X/08/06 0469–12 \$10.00/0 DOI: 10.1177/0021955X08095502

© SAGE Publications 2008

Los Angeles, London, New Delhi and Singapore

KEY WORDS: flexible polyurethane foam, slabstock, flame retardant, melamine.

INTRODUCTION

Polyurethanes (PU) are a versatile class of polymeric materials [1–3]. Rigid PU foams are used for thermal insulation and structural applications [4], whereas flexible PU foams are primarily used as cushioning material with application in furniture, automobiles, and packaging [5]. The foams are prepared by the polymerization of a polyol and a diisocyanate by different catalysts and surfactants. PU foams are particularly easy to ignite and show a high burning velocity. This is due to the high surface-to-mass ratio, high air permeability, open cell structure, low aromaticity, and the high oxygen, carbon, and hydrogen content in the polymer matrix. To meet fire-test requirements it is necessary to protect the polymer with an adequate flame retardant (FR). Currently, the most commonly used FR for flexible PU foam is TCPP [tris-(chloropropyl) phosphate] or deca-BDE (decabromdiphenylether), which are being evaluated by the EU Risk Assessment Body [6] and appear likely to be phased out, along with other halogenated FRs, in the next couple of years. This leads to the increasing application of melamine as a nonhalogenated FR. Like various other FRs, melamine is known to be less effective than halogenated variants, and must therefore have a higher concentration in the PU foam. There are several publications about the flame-retardant effect of melamine in PU foam [7,8]. However, little is known [9,10] about the influence of melamine on the cellular network, the isocyanate chemistry, and the resulting material-specific properties.

EXPERIMENTAL

Materials

In this study, the following materials (Table 1) have been used for manufacturing the flexible PU foams.

Synthesis of the Flexible Standard PU Foam

For synthesis of the flexible PU foam 1 g DMEA, 20.25 g H₂O, 1 g polyetherpolysiloxane (BF 3270), 1 g tin-II-isooctate, and 500 g polyetherpolyol were stirred at 1000 rpm for 1 min. Additionally, 257.5 g toluene diisocyanate TDI 80 was added and the whole mixture was stirred again for 10 s at 2500 rpm. The mixture was then poured into

Table 1. Materials.

Materials	Supplier
Melamine, $d_{50} = 24 \mu\text{m}$, $d_{90} = 37 \mu\text{m}$	BASF AG
Sulphuric acid 96%	Roth GmbH & Co. KG, Germany
Polyetherpolyol Voranol 3322, $M_w = 3500$; OH-number = 46	Elastogran GmbH, Germany
TDI 80, Iso TDI 92290 80%	Elastogran GmbH, Germany
Tolylen-2,4-diisocyanate, 20% Tolylen-2,6-diisocyanate	
Dimethylethanolamine (DMEA), Tegoamin DMEA	Degussa Goldschmidt AG, Germany
Tin-II-isooktoate 100%, Kosmos 29	Degussa Goldschmidt AG, Germany
Polyether-polysiloxane, Tegostab BF 2370	Degussa Goldschmidt AG, Germany
Toluene 99%	Seulberger GmbH & Co.KG, Germany

a 30 cm \times 30 cm \times 30 cm box. Before sample preparation the PU foam was cured for 24 h.

Synthesis of the Flexible PU Foam with Melamine

For preparation of the flexible PU foam with melamine, the necessary melamine content was added to the polyol and mixed with the other ingredients according to the standard procedure. The stirring time of the melamine–polyol composition was individually increased with increasing melamine content. The subsequent synthesis and the sample preparation of the combustion-modified foam were performed in the same manner as the standard PU synthesis. To avoid sedimentation, the polyol–melamine suspension must be used immediately.

Synthesis of the Bisubstituted Urea by Melamine and TDI

A 10 g of melamine were stirred at different temperatures (RT, 60°C, 110°C) in 40 mL toluene for 30 min. Subsequently, 20 μL of the catalyst tin-II-isooktoate and a TDI solution with varying concentration (0.25–4%) were added and stirred for further 2 h. Afterwards the melamine was filtered, washed five times, each time with 10 mL toluene, and dried in the vacuum oven.

Characterization

The viscosity measurements of melamine in polyol were performed by a rotation-rheometer UDS 200 plate/plate from Physica GmbH at 293 K.

To determine the emission according to DIN EN ISO 16000-9, the density according to DIN EN 16021997-01 and compression strength according to DIN ISO 3386-1, a 7 cm × 7 cm × 7 cm cube was cut out from the middle of the 30 cm × 30 cm × 30 cm box. In order to determine the tensile strength and elongation, 2 cm specimens were stamped out parallel to the cube in the box according to DIN 53455. The foaming process was observed according to the foaming qualification system of FOAMAT Typ 281 from Format Messtechnik, Germany. For the FTIR-measurements a FT-IR Magna-IR 750, Nicolet was used.

RESULTS AND DISCUSSION

Synthesis of the PU Foam

The rising profile of the foaming process can be described as a function of exponential decrease first order, with the common formula:

$$y = A \cdot e^{-x/t} + y^0 \quad (1)$$

With increasing melamine content the pre-exponential factor A and the rising height factor y^0 decreased, whereas the factor t increased. This resulted in a decrease in growth and the final rising height with increasing melamine content in the PU formulations. Because the solubility of melamine in the system was quite poor, no chemical influence of melamine, e.g., influence on the PU catalysis, was assumed. These described effects were rather caused by the reduced drainage rate during the cell growth and by the measured reduced temperature in the foaming process:

1. The drainage rate that is driven by the pressure difference in the plateau borders and in the struts, as well as by gravitation, depends on the viscosity in the following manner [11]:

$$\text{Drainage } \alpha \approx \frac{\Delta P}{24\eta} \quad (2)$$

As the viscosity increases, the flow decreases. The viscosity of the polymer should initially be as low as possible for good flow of the polymer out of the struts. But with increasing melamine content the viscosity of the formulation increases, as shown in Figure 1.

With increasing melamine concentration an increasing viscosity is observed. The viscosigram shows an increase of viscosity from

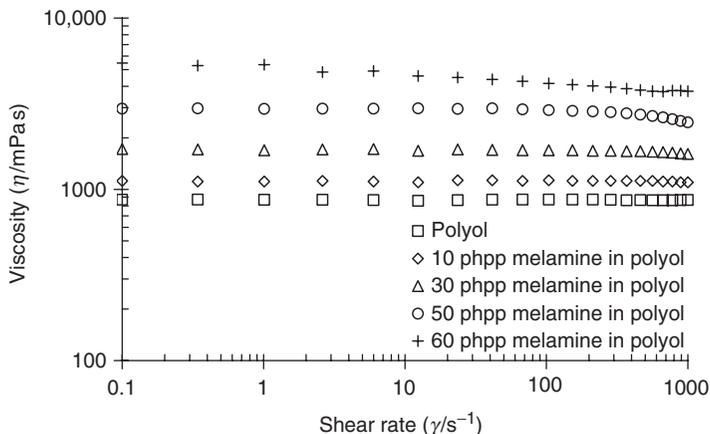


Figure 1. Viscosigram of different concentrations of melamine in polyol.

870 mPas for the pure polyol to 4150 mPas for the 60 phpp polyol–melamine sample. Every curve of the respective melamine concentration shows near-Newton behavior. A low decrease in viscosity at higher shear rates was only observed at higher melamine concentrations (50 and 60 phpp). This indicated a structure viscous behavior of the melamine–polyol suspensions at higher concentrations and shear rates.

Furthermore, a difference in growth and final height between the foaming curve of 20 and 30 phpp melamine in polyol is observed in Figure 2. For the applied melamine contents 20–60 phpp in polyol the volume fractions were calculated in the range of 0.06–0.29 g mL⁻¹. However, the maximum volume fraction was calculated for 0.55 g mL⁻¹. Therefore, the difference was not caused by exceeding the maximum volume fraction. It is rather assumed to be the result of exceeding a viscosity percolation limit in the time-dependent drainage process.

The relationship between the volume fraction, the maximum volume fraction, the intrinsic viscosity, and the resulting viscosity is described by the Krieger–Dougherty equation in the case of spherical particles with the same diameter [12,13].

$$\eta = \eta_0 \left(1 - \frac{\phi}{\phi_{\max}} \right)^{-k \cdot \phi_{\max}} \quad (3)$$

where, η = viscosity of the melamine–polyol suspension, η_0 = viscosity of the polyol, ϕ = volume fraction/g mL⁻¹, ϕ_{\max} = maximum volume fraction/g mL⁻¹, and k = intrinsic viscosity.

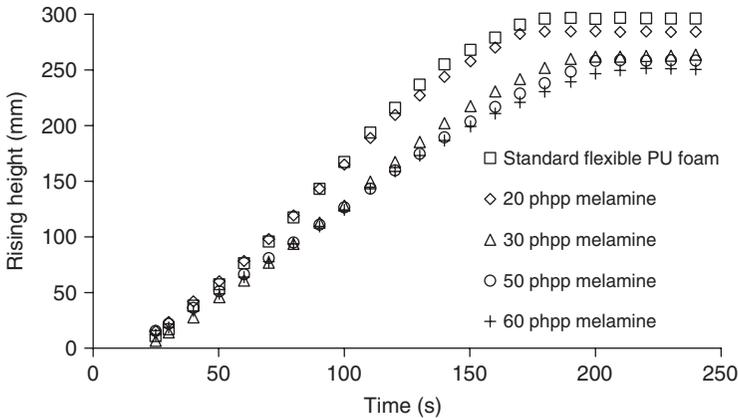


Figure 2. Rising profile of the PU foams with 20, 30, 50, and 70 phpp melamine.

For rigid spherical spheres the value of $k = 2.5$ has a hydrodynamic basis on Einstein [14]. The higher the measured values of the intrinsic viscosity k , the particles show a more irregular geometry resulting in an increase in the resulting viscosity of the suspension. However, the applied melamine particles showed a rather regular geometry. With an empirically determined value of $k = 3.3$, a good correlation of the curve with a coefficient R^2 of 0.982 was found. The exponential curve of the resulting viscosities of the melamine polyol suspensions at a shear rate of $\sim 100 \text{ s}^{-1}$ is pictured in Figure 3.

Therefore, the increase in viscosity is assumed to lead to a decrease in the drainage rate and consequently to a decrease in the rising slope and rising height.

2. With increasing melamine content a decrease in temperature in the foam core during the foaming process was measured. This is caused by the heat capacity of the filled melamine in the PU foam. The specific heat capacity c_p of melamine is with $156 \text{ J g}^{-1} \text{ K}^{-1}$ [15], quite low compared to the unfilled PU foam system. Additionally, the embedding of the melamine particles in the cellular network resulted in broader struts which decrease the heat capacity of the PU system also. The higher the melamine contents in the PU system, the lower is the heat capacity of the whole system which results in a decrease of the temperature in the core of the melamine PU foam. According to the laws of Gay-Lussac the decrease in the temperature resulted in lowering the CO_2 expansion and in a decrease in growth and rising height of the foam and an increase of the foam density and compression strength.

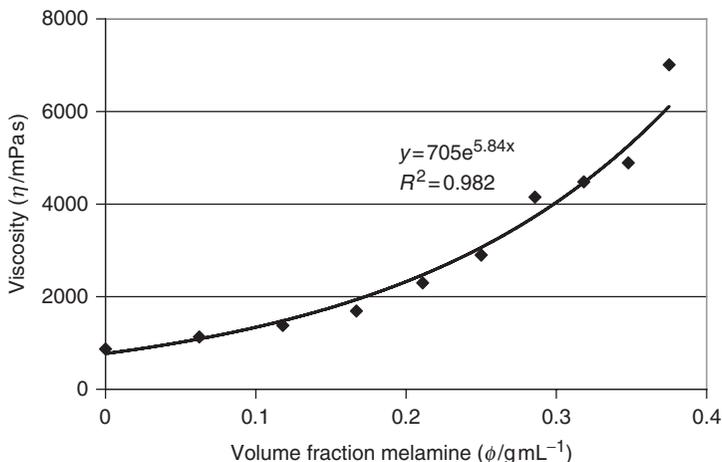


Figure 3. The measured viscosities of the melamine–polyol suspensions in relation to the melamine volume fraction in the range of 0–0.4 g mL^{-1} (0–90 phpp).

Characterization of the Mechanical Properties

The foam structure of PU foam can be differentiated into pores, knots (also called plateau borders), and struts [16]. The pores of the standard flexible foam showed pore diameters of 300–400 μm , knot diameters of 130–150 μm , and strut diameters of 80–100 μm .

Figure 4 shows a dodecahedral cell of a flexible PU foam with 80 phpp melamine where the melamine particles are embedded in the knots and struts. The melamine particle, with a D_{90} of 37 μm , displaced the PU matrix, and the struts and knots were enlarged. The pictured cell shows a pore diameter of ca. 425 μm , a knot diameter of ca. 170 μm and a strut diameter of ca. 120 μm . An optimum distribution for embedding the particles in the knots and in the struts was found for particle sizes from 30 to 100 μm . The applied melamine showed an optimum particle distribution for the embedding in the cellular PU matrix. Melamine with a significantly higher particle size would be too large to embed in the PU cell matrix; the foam would collapse during foaming. Particles with smaller particle size distribution would significantly enhance the viscosity [17].

PU foam-specific parameters of the samples such as density, compression strength, tensile strength, elongation, and air permeability are listed in Table 2.

Yet low amounts of melamine (e.g., 20 phpp melamine) resulted in a strong change of the mechanical properties. With increasing melamine

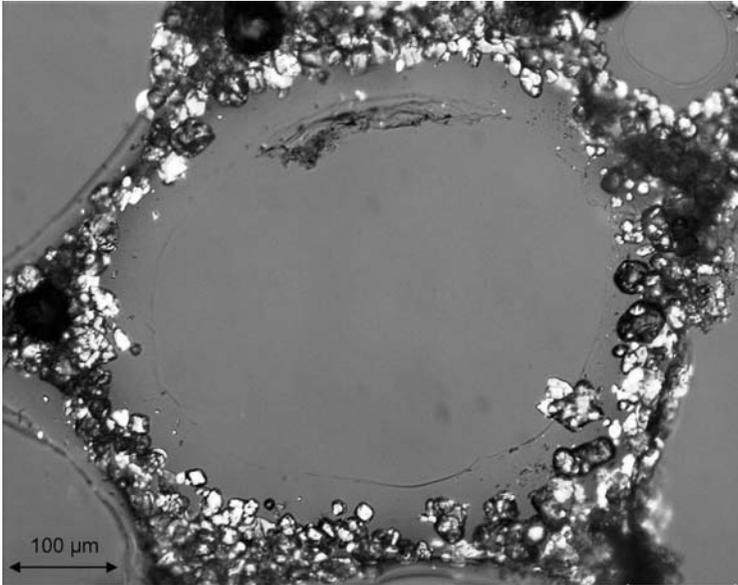


Figure 4. Polarization microscopy of 80 phpp melamine in flexible PU with the visible crystalline melamine particles.

Table 2. Mechanical properties of the resulting PU foams with melamine as flame retardant.

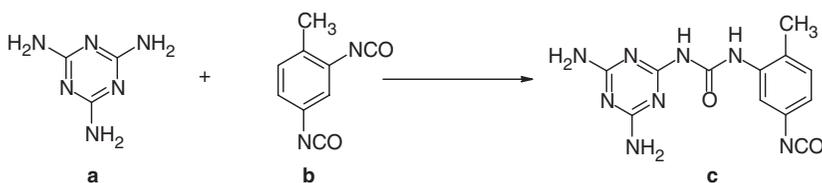
	Density δ (kg m^{-3})	Compression strength cv (kPa)	Tensile strength σ (kPa)	Elongation ϵ (%)	Air permeability ($\text{dm}^3 \text{min}^{-1}$)	Number of cells (cm^{-1})
Standard flexible PU	25	4.7	0.13	228	3.2	19.3
20 phpp melamine	27.9	5.4	0.07	102	2.6	15.7
30 phpp melamine	30.4	6.0	0.05	57	2.5	14.3
40 phpp melamine	32.3	7.1	0.06	66	2.1	16.7
50 phpp melamine	33.8	7.9	0.06	49	2.0	14.3
60 phpp melamine	37.3	9.2	0.05	37	1.9	13.7

content the density of the resulting foams increased from 25 to 37.3 kg m^{-3} , which is caused by the weight of the incorporated melamine particles and the reduced foaming height. Additionally, the values of the compression strength nearly doubled. Thus, the melamine particle showed a strong stiffening effect on the cellular network by broadening the struts and knots.

This embedding of the melamine in the PU matrix on the one hand and the limited drainage caused by the increased viscosity on the other

hand resulted in a decrease in the number of cells from 19.3 to 13.7 on average, and a decrease in the air permeability from 3.2 to $1.9 \text{ dm}^3 \text{ min}^{-1}$. The decrease in air permeability caused by the reduced drainage rate at unfilled molded foams was also discussed by Turner et al. [18]. Instead an increase in the number of cells caused by the more intensive nucleation of the forming CO_2 on the surface of the particles was not measurable. Therefore, the applied melamine concentration of 20 phpp was assumed to be too high. In addition, the values for the tensile strength and elongation decreased significantly. Already, small concentrations of melamine strongly decreased the elasticity of the resulting foams. The melamine particles worked like a predetermined breaking points and inhibited the complete elongation.

The chemical structure of melamine shows a triazine ring with three amino groups. According to Oertel [1] the amino group is known to be approximately three times more reactive than the hydroxyl groups of the polyols. Because of the insolubility of the melamine only amino groups on the particle surface are assumed to react with the isocyanate to form melamine-based bisubstituted urea.



This mechanism has been proposed in literature [19,20] but not verified yet. In order to study this suggested mechanism, samples were treated according to the procedure described in Synthesis of the Bisubstituted Urea by Melamine and TDI section. The products of the described procedure were measured by FTIR, pictured in Figure 5.

In Figure 5, the melamine sample that was treated with 40 ppm TDI with a catalyst at room temperature shows a similar spectrum compared to the spectrum to the untreated melamine sample. There is only a weak absorption peak at 2299 cm^{-1} . This absorption that indicates an N–H stretching vibration, can be attributed to the asymmetric stretching vibration of the NCO group of the TDI. Pure TDI shows very strong, broad signals at 2279 cm^{-1} . The shift to higher wave numbers (20 cm^{-1}) could be explained by the low intensity of the signal. Thus, the formation of the melamine-based bisubstituted urea was not detected. Further investigation of the products obtained from the reaction between melamine and TDI was not possible. This is due to the insolubility of melamine in toluene resulting in a surface reaction. Thus, the urea

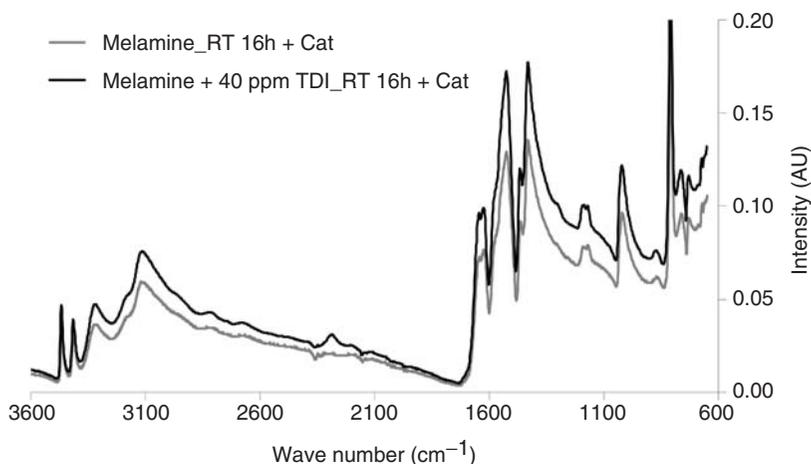


Figure 5. FTIR-spectrum of the melamine sample treated with 40 ppm TDI with a catalyst at room temperature in comparison to an untreated melamine sample.

derivatives only form on the surface of the melamine particles and cannot be analyzed with ¹H- and ¹³C-NMR spectroscopy. Future studies should focus on chromatographic analyses of molecular products and/or surface analytical methods such as ESCA (Electron Spectroscopy for Chemical Analysis, XPS).

CONCLUSION

In order to understand the influence of melamine in flexible PU foam for slabstock applications, different amounts of melamine in the range of 20–90 phpp were investigated. The rising profile of the PU foam synthesis, which follows an exponential function, showed a strong dependence on the melamine content. With increasing melamine content, a decrease in growth and the final rising height was measured. First, these effects were caused by the increased heat capacity of the foam, which results in lower temperatures in the foam and finally a decrease in expansion of the cell gas CO₂. Second, the melamine showed a strong influence on the viscosity. Melamine–polyol suspensions show viscosities in the range of 870 mPa s for the pure polyol to 4150 mPa s for the 60 phpp polyol–melamine sample. This increase in viscosity significantly influences the time-controlled drainage rate. The drainage rate was reduced which caused a reduced thinning of the struts and a reduced expansion of the cell gas CO₂. Furthermore, at higher melamine

contents (50 and 60 phpp) at higher shear rates a structure viscous behavior of the melamine–polyol suspensions was measured. With a measured value of $k=3.3$ of the Dougherty–Krieger equation a good correlation of the curve with a coefficient R^2 of 0.982 was found. The applied melamine with a D_{90} value of $37\ \mu\text{m}$ showed an optimum distribution for embedding in the struts and plateau borders of the cellular PU foam. The density of the resulting foams increased with increasing melamine content because of the incorporated particles and the reduced foaming height. Additionally, the compression strength increased in the same way, caused by the stiffening effects of the melamine particles in the cellular network with the broadened struts and knots. By contrast, the number of cells and the air permeability decreased with increasing melamine content caused by the reduced drainage rate mentioned above. Furthermore, FTIR experiments were performed for studying the formation of a bisubstituted urea by TDI and melamine at the particle surface. The spectra of the TDI-treated melamine showed no difference to the untreated melamine. Thus, the formation of the melamine-based urea was assumed to be rather improbable.

REFERENCES

1. Oertel, G. (1994). *Polyurethane Handbook*, **2nd edn**, Hansa, Munich.
2. Randall, D. and Lee, S. (2002). *The Polyurethanes Book*, **1st edn**, Wiley, New York.
3. Woods, G. (1990). *The ICI Polyurethanes Book*, **2nd edn**, Wiley, Everberg and Chichester.
4. Kumaran, M.K. and Bomberg, M.T. (1990). Thermal Performance of Sprayed Polyurethane Foam Insulation with Alternative Blowing Agents, *Journal of Building Physics*, **14**(1): 43–57.
5. Chao, C.Y.H. and Wang, J.H. (2001). Transition from Smoldering to Flaming Combustion of Horizontally Oriented Flexible Polyurethane Foam with Natural Convection, *Combustion and Flame*, **127**(4): 2252–2264.
6. Risk Assessment Report on Tris(2-Chlor-propyl) Phosphate (TCPP), Scientific Committee on Health and Environmental Risks, Environmental Part, EINECS No. 237-158-7, 2007.
7. Schrock, A., Solis, R., Beal, G.E., Skorpenske, R.G. and Parish, D.B. (1989). The Influence of Polymer Morphology and Density on the Combustion of Melamine-Filled Flexible Polyurethane Foams, In: *Proceedings of the SPI Annual Technical/Marketing Conference*, San Antonio, Texas.
8. Vanspeybroeck, R., Van Hess, P. and Vandeveldel, P. (1993). Combustion Behaviour of Polyurethane Flexible Foams under Cone Calorimeter Conditions, *Fire and Materials*, **17**(4): 155–166.

9. Craig, T.A., Lear, J.J. and Motte, P. (1993). New Generation Flame Retardant Polyols for Slab-Stock Applications, In: *Polyurethanes World Congr. Proc.*, 54-9, Technomic, Lancaster, PA.
10. Scaccia, C., Fisher, D.H. and Throckmorton, P.E. (1987). Stable Polyol-Melamine Blend for Use in the Manufacture of Fire Retardant Flexible Urethane Foam, Patent number 4644015.
11. Bikerman, J.J. (1953). *Foams: Theory and Applications*, Reinhold, New York.
12. Krieger, I.M. and Dougherty, T.J. (1959). A Mechanism for Non-Newtonian Flow in Suspensions of Rigid Spheres, *Trans. Soc. Rheol.*, **3**(1): 137-152.
13. Dougherty, T.J. (1959). Ph.D. Thesis, Case Institute of Technology.
14. Einstein, A. (1905). Motion of Suspended Particles in Stationary Liquids Required from the Molecular Kinetic Theory of Heat, *Ann. Physik*, **17**: 549-560.
15. Stephenson, C.C. and Berets, D.J. (1952). The Heat Capacities and Entropies of Melamine and Dicyandiamide, *Journal of the American Chemical Society*, **74**: 882.
16. Weaire, D. and Hutzler, S. (1999). *The Physics of Foams*, **1st edn**, Clarendon Press, Oxford.
17. Kageoka, M., Tairaka, Y. and Kodama, K. (1997). Effects of Melamine Particle Size on Flexible Polyurethane Foam Properties, *Journal of Cellular Plastics*, **33**(3): 219-237.
18. Turner, R.B., Nichols, J.B. and Kuklies, R.A. (1988). The Influence of Viscosity in Cell Opening of Flexible Molded Foams, In: *Proceedings of the SPI, 31st Conference*, Technomic, Lancaster, PA.
19. Dick, C.M., Denecker, C., Liggit, J.J., Mohammed, M.H., Snape, C.E., Seely, G.C. et al. (2002). Solid State ¹³C and In Situ ¹H-NMR Study on the Effect of Melamine on the Thermal Degradation of a Flexible Polyurethane Foam, *Polym. Int.*, **49**: 1177-1182.
20. Price, D., Liu, Y., Milnes, G.J., Hull, R., Kandola, B.K. and Horrocks, A.R. (2002). An Investigation into the Mechanism of Flame Retardancy and Smoke Suppression by Melamine in Flexible Polyurethane Foam, *Fire and Materials*, **26**(4): 201-206.