Polyurethane Foams from Melamine Solutions in Reactive Solvents Based on Ethyl Methyl Ketone

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ABSTRACT: This work presents conditions and method for obtaining foamed melamine–formaldehyde–butanone (Mel-F-MEK) materials of improved thermal stability. They were obtained from melamine solution in reactive solvents based on ethyl methyl ketone and 4,4′-diphenylmethane diisocyanate. Some properties of obtained polyurethane foams were examined, e.g., apparent density, water absorption, dimensional stability, thermal conductivity, flammability, as well as static and dynamic thermal stability and compressive strength. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012
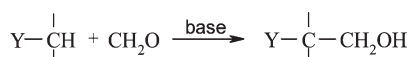
INTRODUCTION

Reactive solvents are the hydroxymethyl derivatives of aliphatic compounds with electronegative groups activating the C—H bond in the α-position. They are obtained in an alkaline environment in additional reactions of formaldehyde to aliphatic C—H bond, activated by strongly electronegative group (Y), such as carbonyl or nitro group.[1]

$$Y{-}\overset{|}{\underset{|}{C}}H + CH_2O \xrightarrow{\text{base}} Y{-}\overset{|}{\underset{|}{C}}{-}CH_2OH$$

The concept of reactive solvents was the first time introduced by Z. Wirpsza, who noticed that the melamine dissolves not only physically but also in the solution it reacts with the obtained product and creates a reactive system similar to resin.[2] The most important feature of the reactive solvents is possibility to dissolve sparingly soluble compounds (e.g., melamine) in organic solvents. This creates the possibility of obtaining new solid[3,4] and filled[5] materials or polyurethane foams.[6]

In the literature, there is no information on the use of melamine reactive solvents for the production of polyurethane foams with the exception of the work,[7] in which foaming process was carried out at elevated temperature with addition of chemical blowing agents [azodicarbonamide (ADN) and sodium bicarbonate]. Melamine foams foamed with NaHCO₃ have less uniform structure than foams foamed with ADN, but they are more resistant to heat. Foams foamed with ADN are characterized by a completely uniform cellular structure and smaller size of cells.

Lack of information on the preparation of polyurethane foams at room temperature without using of aforementioned blowing agents was the cause of research carried out in this direction, and it indicates the new possibilities of application of reactive solvents of melamine.

In some applications, thermal strength of traditional polyurethane foams (90–120°C) is insufficient. Sometimes, however, materials of increased thermal stability are required.[8] It was supposed that foams obtained from melamine–formaldehyde–ketone resins should be such materials due to the presence of thermally stable *s*-triazine ring. Those assumptions were confirmed in the work,[6] where cyclohexanone (CH) was used as the initial keton (being the integral part of melamine–formaldehyde–cyclohexanone (Mel-F-CH) resin.

The foaming agent was carbon dioxide formed in the reaction between water and isocyanate groups. Obtained foams were of rigid and semirigid type—the presence of ring in CH makes the molecule rigid by increasing the number of rigid segments.

This work, which continues research on obtaining foamed polyurethane materials, is focused on methyl ethyl ketone (MEK, butan-2-on). Aliphatic chain present in its structure increases the number of flexible segments. Foams were obtained from 4,4′-diphenylmethane diisocyanate (MDI) and melamine–

formaldehyde–butanone (Mel-F-MEK) resins obtained from melamine solutions in reactive solvents (obtained in reactions of 1 mol MEK with 5 or 7 mol formaldehyde).

There were obtained self-extinguishing polyurethane foams containing the s-triazine ring. They are characterized by better thermal stability and increased compressive strength after thermal exposure in comparison to conventional polyurethane foams.

EXPERIMENTAL

Chemicals

MEK (ethyl methyl ketone) (CHEMPUR, Piekary Śląskie, Poland); formalin (STANDARD, Lublin, Poland); melamine (FLUKA, Buchs, Switzerland); MDI (4,4′-diphenylmethane diisocyanate) (MERCK, Germany); Silicone 5340 (Houdry Hülls); Triethylamine (FLUKA, Buchs, Switzerland).

Preparation of Reactive Solvents

Reactive solvents were obtained in reactions of 1 mol MEK with 5 or 7 mol formaldehyde as per the formula specified in the work.[1] Obtained products were designated 5-HMMEK and 7-HMMEK. The reactive solvents were prepared in a three-necked 250-cm^3 flask equipped with reflux condenser, thermometer, and mechanical stirrer from predetermined amounts of MEK and formalin (34% of CH_2O). Typically, 1 mol of ketone was reacted with 5 or 7 mol of formaldehyde. Triethylamine was then added to adjust pH to 11. The reaction was carried out at 80°C for 8–10 h. After that time, water and catalyst was removed by distillation under reduced pressure.

To assess the degree of conversion of the substrates in the reaction of MEK with formaldehyde, the mass balance was performed with an accuracy of ±0.1 g: substrates before the reaction, reaction mixture, and products obtained after separating water and the catalyst by distillation.

Obtaining Melamine Solutions in Reactive Solvents

Melamine solutions in reactive solvents were obtained because of solubilization of one-time added melamine to anhydrous 5-HMMEK and 7-HMMEK. The amount of melamine resulted from previous solubilization tests was the maximum (or nearly maximum) amount not causing gelation of the solution.[9] The mixture was heated until the complete digestion of the compound, stirring with a thermometer and noting down the temperature of its dissolution (90 ÿ ¡ 110°C). The maximum amount solubilized was 30.0 g per 100 g 5-HMMEK and 33.3 g per 100 g 7-HMMEK (regardless of type of used of reactive solvent).

Obtaining Polyurethane Foams

Melamine solutions in 5-HMMEK and 7-HMMEK were foamed at room temperature, on a small scale, as in the work.[6] Foaming of melamine solutions in reactive solvent (RS) was carried out at room temperature, on a small scale, in cardboard cups of 200 cm^3. The following was added to the cup: (i) solution of melamine in 5-HMCH or 7-HMCH (as a polyol agent), (ii) silicon 5340 (as surfactant), (iii) triethylamine (as catalyst), (iv) water (as a foaming agent), and (v) MDI (as isocyanate agent). Indicative amount of MDI required to obtain polyurethane foam was calculated as per eq. (1) and was later adjusted empirically (subsequently corrected by experiments).

$$m_{NCO} = \left[\frac{42 \cdot m_{mixt.}}{p_{NCO}} \left(\frac{100 \cdot f_{mixt.}}{M_{mixt.}} + \frac{P_{H_2O}}{18} \right) \right] \cdot k \quad (1)$$

where m_{mixt} is the weight (g) RS and Mel used for foaming. M_{mixt} is the average molar mass (g mol^{-1}) of the mixture. f_{mixt} is the average functionality of the mixture. p_{H2O} is the content (wt %) of water as related to the weight of RS used. p_{NCO} is the content (wt %) of ─NCO groups in isocyanate, required to react with RS. k is the isocyanate coefficient determining mole ratio of ─NCO groups to ─OH groups.

When all components were added to the cup, they were energetically stirred until creaming began. Measured durations: (i) creaming (commencement time, obtaining the so-called creamy consistency, i.e., time from mixing of components to beginning of volumetric expansion). (ii) expansion (time from the beginning of expansion to reaching by foam its maximum volume), and (iii) drying of foam (time from reaching by foam its maximum value to the moment when loose materials no longer adhere to the surface). Such polyurethane foams were then cut to shape and used for further tests.

Testing the Properties of Obtained Polyurethane Foams

The Apparent Density. The apparent density of foams was determined according to ISO 845:2010 (Rubber and porous plastics: Determination of the apparent density). For research purposes, the samples were cut out in the shape of a cube with 50-mm edges. Initially, the foams were seasoned within 24 h at room temperature and then the samples were cut out from the foams with an accuracy of up to 0.1 mm and weighed with an accuracy of up to 0.1 g.

The Dimensional Stability. The dimensional stability of foams was examined to standard ISO 2796:1986 (Rigid porous plastics: Examination of dimensional stability). For research purposes, the samples were cut out in the shape of a cube with 50-mm edges The change in linear dimensions (Δl) of the examined foams, after periods of 20 and 40 h from the time of thermal exposure at the temperature 150°C, was calculated based on eq. (2), measuring in the foam rise direction:

$$\Delta l = \frac{l - l_0}{l_0} \cdot 100\% \quad (2)$$

where l_0 is the sample length before thermal exposure and l is the sample length after thermal exposure.

The Water Absorbing Capacity. The water absorbing capacity was carried out in accordance with ISO 2896:1987 (Rigid porous plastics: Determination of water absorbing capacity), specifying the volume of water absorbed by the sample. The samples in the shape of a cube with 50-mm edges were cut out from the obtained foams, and then weighed with an accuracy of 0.1 g. The fittings thus prepared were subsequently immersed in distilled water and clamped tight with a glass cork. The measurement was made at ambient temperature. After periods of 5 min, 3 h, 6 h, and 24 h, the samples were taken out of the jars and weighed. Water absorption is expressed as the percentage ratio of the absorbed water volume to the initial sample volume.

The Infrared Spectrum. IR spectrum obtained for selected polyurethane foam was recorded by horizontal attenuated total reflectance (ATR) on a store brand by Bruker (ALPHA) Fourier transform infrared spectroscopy (FT-IR) spectrometer (Bruker). The sample was prepared in the form of KBr tablet.

The Static Thermal Stability. The static thermal stability (resistance) of foams was assessed based on the percentage of mass loss after heating at temperatures 150, 175, and 200°C in air atmosphere for 30 days. The thermal stability (expressed in weight percent) was calculated from eq. (3):

$$\Delta m = \frac{m_1 - m_2}{m_1} \cdot 100\% \qquad (3)$$

where m_1 is the sample mass before thermal exposure (g), and m_2 is the sample mass after thermal exposure (g).

The Dynamic Thermal Resistance. Thermal analysis of foams was performed to standard ISO 11358:2004 [Plastics, Thermogravimetry (TG) of polymers], General principles [using derivatograph F. Paulik, J. Paulik, L. Erdey (Hungary)] under dynamic conditions in air at temperatures ranging from 20 to 800°C (heating rate 5°C min^{-1}, amplification: differential thermal analysis (DTA) 1/15°; differential thermogravimetric (DTG) 1/10°). The results were recorded as DTA, DTG, and TG curves.

The Compression Strength. The compression strength was determined in accordance to standard ISO 844:2010 (Rigid porous plastics: Compression test on rigid porous plastics). It was examined using the testing machine FT 100, produced by Heckart (Germany). The samples in the shape of cubes with 50 ± 1-mm edges, after removing the skin and sides, were cut out from the foams and subjected to 10% compressive deformation in the foam rise direction.

The Thermal Conductivity. The thermal conductivity of the foams was determined by examining the thermal conductivity coefficient λ using the ISOMET 2114 device (Applied Precision, Slovakia). A needle probe was inserted in the tested sample to perform the measurement. The heat impulse is generated in the device, by heating the resistance wire. The device optimizes the parameters and performs measurements by measuring the probe temperature on a continuous basis. The probe remains in close contact with the tested material.

The Flammability. The flammability of foams was determined by test in horizontal position according to official procedure PN-C-89023:1982 (Plastics: Examination of flammability of plastics in the form of bars) (Ed. Polish Committee for Standardization).

The Speed of Flame Propagation on Surface. The speed of flame propagation on surface was determined to standard PN-C-05012-12:1978 (Methods for examination of porous plastics: Determining the speed of flame propagation on surface) (Ed. Polish Committee for Standardization). Measurements were carried out for a dozen or so random samples of materials.

RESULT AND DISCUSSION

Polyurethane foams were obtained from melamine solutions in reactive solvents based on MEK (polyol agent) after adding silicon 5340 (surfactant), triethylamine (catalyst), water (foaming agent), and MDI (isocyanate agent).

Anhydrous reactive solvents (RS) obtained as a result of reaction of 1 mol MEK with 5 or 7 mol formaldehyde, were used in tests. Mel-F-MEK resins, constituting (with MDI) the major components for production of polyurethane foams, were obtained by solubilization in them of melamine (in maximum amount that would not cause gelation).

Foaming Conditions
Content of the composition is listed in Table I. The tests aimed at determination of effects of melamine, catalyst triethylamine (TEA), isocyanate (MDI), foaming agent (water) amount, and reactive solvent type to foaming process (Table I).

It was determined that the optimum amount is 1.5–3.2 wt % of water as related to RS weight. Adding larger amount of water significantly extends foaming time, reduces apparent density of foam, and its strength properties. The amount of added catalyst (TEA) is also a very important factor. In the case of foams obtained from melamine solutions in 5-HMMEK and 7-HMMEK, it is 0.9–2.7 g per 100 g RS. The use of larger amounts of both water and a catalyst (>3 g/100 g RS) fosters the formation of shorter polymer chains, increasing the foam fragility, and thus adversely affecting their mechanical properties.

Failure to meet the optimum foaming conditions results in produced foams showing very high polymerization contraction during heating (very high isocyanate content), insufficient foaming (very low water content), with irregular pores (very high water content), or not afterbaked (very low isocyanate content).

In addition, thermal stability of foams was tested by mass loss method. It was determined that the best foams are obtained using such amount of isocyanate that mole ratio of isocyanate groups to hydroxyl group in initial reactive mixture (isocyanate coefficient) is 0.8–1.0. When the coefficient was lower, below 0.8, foams with sticky surface were obtained, indicating their incomplete crosslinking. When a little more of isocyanate (coefficient higher than 1.0) was added, foams with very large polymerization contraction and lower thermal strength were obtained as a result of incomplete isocyanate conversion. The optimum isocyanate coefficient for Mel-F-MEK resins was, respectively, 0.8–0.9 for melamine solutions in 5-HMMEK and 0.9–1.0 for melamine solutions in 7-HMMEK.

Properties of Foams
Foamed materials obtained from melamine solutions in 5-HMMEK and 7-HMMEK feature lower rigidity than those obtained from 5-HMCH and 7-HMCH (see Ref. 6). This is due to the structure of initial ketones: the ring present in CH stiffens the molecule (by increasing the number of rigid segments), whereas aliphatic chain present in MEK increases the number of flexible segments. It is to be mentioned that heating of melamine foams (at temperature > 100°C), which at room temperature, is semirigid, for a couple of hours makes them rigid. The heating of foams at elevated temperature increases their rigid due to the postcuring of composition because of additional crosslinking.

Table I. Effect of Composition on Foaming Process

Reactive solvent	Symbol of composition	Content of composition[a] (g/100 g RR)				Foaming process[b]			Foam characteristics directly after obtaining
		Melamine	Isocyanate (MDI)	Catalyst (TEA)	Water	Creaming time (s)	Expansion time (s)	Drying time (s)	
5-HMMEK	A1	23.3	180.0	2.7	0.4	19	60	400	D
	A2	23.3	180.0	1.9	2.8	15	75	700	D
	A3	23.3	180.0	0.4	1.4	30	100	240	ND
	A4	23.3	180.0	1.1	0.4	20	66	240	D
	B1	26.7	200.0	2.7	0.4	23	80	360	D
	B2	26.7	200.0	1.9	2.8	15	82	120	ND, DS
	B3	26.7	200.0	1.1	0.4	30	65	60	D
	C1	30.0	220.0	2.7	0.4	25	105	600	D, DS
	C2	30.0	220.0	–	1.4	25	92	60	ND
7-HMMEK	D1	23.3	120.0	2.3	0.4	27	96	420	D, DS
	D2	23.3	120.0	–	1.4	25	71	620	ND
	D3	23.3	120.0	0.2	1.4	20	50	700	D, DS
	E1	26.7	130.0	0.2	0.4	40	147	900	ND, DS
	E2	26.7	130.0	0.4	0.8	30	90	600	D
	F1	30.0	135.0	1.9	1.4	25	90	480	ND
	F2	30.0	140.0	1.9	0.4	32	150	300	D, DS
	F3	30.0	145.0	0.4	1.4	26	113	120	D
	F4	30.0	145.0	1.5	0.4	20	80	120	D
	F5	30.0	145.0	0.8	0.4	30	114	300	D, MS
	F6	30.0	150.0	–	1.4	33	130	120	D
	G1	33.3	160.0	0.4	0.4	30	180	900	ND
	G2	33.3	160.0	0.2	0.4	35	125	480	D, DS
	G3	33.3	160.0	0.4	1.4	40	120	480	D

Creaming time is the time from mixing of components to beginning of volumetric expansion. Expansion time is the time from the beginning of expansion to reaching by foam its maximum volume. Drying time is the time from reaching by foam its maximum value to the moment when loose materials no longer adhere to the surface.
[a]Always the same amount of surfactant 0.9 g/100 g RS was added, [b]Component mixing time about 10 s.
D, afterbaked foam; ND, not afterbaked foam; MS, small polymerization contraction; DS, large polymerization contraction.

The structure of obtained foams was confirmed based on analysis of IR spectra. It can be concluded that the structure of polyurethane foams contains also carbodiimide groups (2136 cm^{-1}), which increase the thermal resistance of foam (decomposition temperature > 270°C).[10] The carbonyl group occurring in different molecular environments in the structure of polyurethane foam absorbs at about 1700 cm^{-1}, and the ester bond ─COO─ appears at around 1230 cm^{-1}. The band occurring at 812 cm^{-1} confirms the presence of the 1,3,5-triazine ring in the structure of the foam. In addition, in the IR spectrum of tested foams, there are bands at 3418 and 1530 cm^{-1} (the secondary amide band), characteristic for vibrations of NH groups.

Some selected basic properties of obtained foams were examined, i.e., apparent density, water absorption, dimensional stability, thermal stability, flammability, speed of flame propagation on surface, and compression strength. Apparent density of foamed melamine materials obtained from melamine solutions in 5-HMMEK and 7-HMMEK does not exceed 36.0 kgm^{-3} (Table II). It is lower than in the case of foams obtained from Mel-F-CH resins containing a heavier CH ring. It is also lower

than density of foams produced (in the same conditions) from polysterols obtained from isocyanuric acid (IA) and oxiranes.[8]

Water absorption is within the range 0.1–3.9% vol (after 3 h) and 0.7–6.4% vol (after 24 h of immersion) and is lower than that of foams obtained from IA (3.0–6.9% vol after 3 h and 4.0–7.9% vol after 24 h of immersion) (Table II).

Foamed melamine materials feature dimensional stability. In the case of best foams, change in linear dimensions reached 0.0–1.5% (Table II) and was little lower or comparable to results for foams of IA (0.2–0.3% vol).[8]

Foam properties differ due to the structure of reactive solvent. It was determined that at increased temperature (>120°C in exothermic reaction with isocyanate), reactive solvents containing in their structure small amount of unstably bonded formaldehyde release formaldehyde, which might cause breaking of foam pores and increasing water absorbing capacity. In addition, there is a possibility of formaldehyde release during heating, which in turn increases foam contraction.

Table II. Selected Properties of Foams Obtained from Melamine Solutions in 5-HMMEK and 7-HMMEK (Measured at temperature 20°C) (Marking as per Table I)

Reactive solvent	Symbol of composition	Apparent density ρ_p (kg m^{-3})	Change in linear dimensions (linear %)	Water absorbing capacity (vol %) after	
				3 (h)	48 (h)
5-HMMEK	A1	22.5	0.0	1.0	1.8
	A2	18.5	0.2	1.4	1.7
	A3	13.7	1.0	0.6	1.7
	A4	17.8	0.0	1.4	2.3
	B1	19.1	0.0	1.2	2.4
	B2	31.3	0.0	2.8	6.3
	B3	28.7	1.2	2.3	3.6
	C1	36.0	1.2	1.6	2.7
	C2	18.6	1.5	3.0	4.5
7-HMMEK	D1	21.4	0.3	1.3	2.1
	D2	37.5	1.1	3.9	6.1
	D3	31.6	0.3	2.2	4.1
	E2	18.0	1.3	1.8	2.3
	F1	28.2	1.2	0.1	2.3
	F3	21.0	0.9	0.1	0.7
	F2	12.0	0.2	0.2	0.7
	F4	17.6	0.0	0.7	3.5
	F5	30.3	0.0	0.7	0.9
	F6	16.8	0.2	0.5	0.9
	G1	27.3	0.9	3.5	5.3
	G2	26.9	0.7	3.9	6.4
	G3	22.8	0.1	1.1	1.5

Thermal Stability of Foams

Tests of thermal stability carried out at temperatures 150, 175, and 200°C by measuring of mass loss (Figures [1–3]) and assessing, preliminarily, mechanical properties of foams (Table III). Changes of mass of selected foams, in the function of time and exposure temperature, are shown in diagrams; Figure 1 refers to foams obtained from melamine solutions in 5-HMMEK and Figure 2 to composition with 7-HMMEK. Successive mass loss of foams was observed during heating, and the highest mass loss was observed within first 24 h. Foams obtained from Mel-F-MEK resins show (depending on temperature) mass loss equaling, respectively, 13.7–19.0 wt % for 7-HMMEK and 23.0–31.0 wt % for 5-HMMEK. They are higher than in the case of compositions obtained from Mel-F-CH resins.[6]

Foams obtained from melamine solutions in 5-HMMEK show lower thermal stability, which is probably due to the presence in foam structure of larger number of unstable oxymethylene units ($-O-CH_2-$), which at an increased temperature might undergo degradation, accompanied with release of formaldehyde, to the following reaction[8,10]:

$$\text{N} \equiv \text{NH-CH}_2\text{-O-CH}_2\text{-NH-} \xrightarrow{\text{temp.}} \text{N} \equiv \text{NH-CH}_2\text{-NH-} + \text{CH}_2\text{O}$$
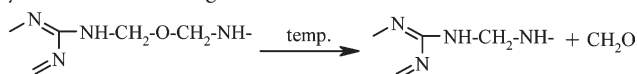
The thermal stability (measured at temperature 200°C by mass loss method) of example compositions obtained from Mel-F-

MEK resins is shown in Figure 3. Foams obtained from melamine solutions in 7-HMMEK show lower mass loss than compositions with 5-HMMEK, which is probably due to better crosslinking of the former. Compositions obtained from Mel-F-MEK resins show higher mass loss than those of Mel-F-CH resins, in which the cyclohexanone ring is more resistant to thermal decomposition.[6]

Changes in mass of melamine foams were, in majority of cases (except 5-HMMEK), comparable to changes in mass of foamed polyurethane materials obtained from IA.[8] The advantage of compositions obtained from Mel-F-MEK resins is higher rigidity after heating and much higher compression strength after exposure at temperature 150, 175, and 200°C. Changes in those properties are due to the reaction of additional networking which occurs at high temperatures and the presence of stable s-triazine ring. Additional information on stability (i.e., thermolytic and thermo-oxidation stability) of foamed plastic are provided by differential thermal analyses (DTA, DTG, and TG).

Thermograms of selected foamed melamine materials (Figure 4) indicate that thermal degradation process comprises several stages. At temperature up to 150°C, a 1–3% sample mass loss is observed; this is probably due to release of formaldehyde from O-hydroxymethyl groups $-O-CH_2OH$. At temperature ~160°C, dissociation of hydrogen bonds in rigid segments

Table III. Compressive Strength of Foams Obtained from Melamine Solutions in 5-HMMEK and 7-HMMEK (Marking as per Table I)

| Reactive solvent	Symbol of composition	Before heating	Compression strength (MPa) After heating in temperature			Increase of compression strength (%) (compared with composition before heating) after heating at temperature		
			150°C	175°C	200°C	150°C	175°C	200°C
5-HMMEK	A3	0.035	0.047	0.051	0.043	34.3	45.7	22.8
	B1	0.052	0.065	0.070	0.064	25.0	34.6	23.1
	B2	0.072	0.084	0.096	0.094	16.7	33.3	30.5
	B3	0.046	0.067	0.085	0.089	45.6	84.8	93.5
	C1	0.033	0.054	0.061	0.063	63.6	84.8	90.9
	C2	0.045	0.094	0.113	0.080	108.9	151.1	77.8
7-HMMEK	E2	0.047	0.080	0.066	0.057	70.2	40.4	21.3
	D1	0.044	0.061	0.058	0.050	38.6	31.8	13.6
	D2	0.026	0.034	0.038	0.046	30.8	46.2	79.6
	F1	0.020	0.033	0.030	0.026	65.0	50.0	30.0
	G2	0.021	0.034	0.044	0.052	61.9	109.5	147.6
	G3	0.020	0.033	0.042	0.036	65.0	110.0	80.0

occurs. Depending on the type of composition, 5% foam weight loss is observed at temperature 160–200°C, 10% at 180–220°C, with the maximum degradation at ∼350°C. DTA curve shows a clear endothermic peak of melamine *s*-triazine ring degradation at temperature of ∼350°C. TG curve shows the kink, with corresponding weight loss on DTG curve due to ring destruction. Above that, temperature thermogram shows a broad exothermic peak, with corresponding successive weigh loss on TG curve. The peak indicates the occurrence of oxidation (thermo-oxidation) process of foam degradation products. At temperature above 700°C, degradation process is almost finished, with foam mass approaching zero.

Compression test were performed on foams obtained directly and after the exposure to temperature 150, 175, and 200°C (Table III). It was observed that all tested foams, after heating

at temperature 150 and 175°C, featured higher rigidity and much higher compression strength, which is due to the cross-linking of foam at elevated temperatures. Foams exposed to heat at temperature 200°C also improved their compression strength, only to the lower extent.

Having listed the results from the foams from Mel-F-MEK resins with results for foams of Mel-F-CH resins (see Ref. 6), it was determined that the latter showed higher compression strength (as well as thermal stability), which is due to the presence of the cyclohexanone ring.

Based on the compression test of foams obtained from Mel-F-MEK resins (before to exposure at increased temperature), they can be classified as semirigid foams. In the case of foamed materials of Mel-F-CH resins, foams were classified as semirigid and rigid.[6,10]
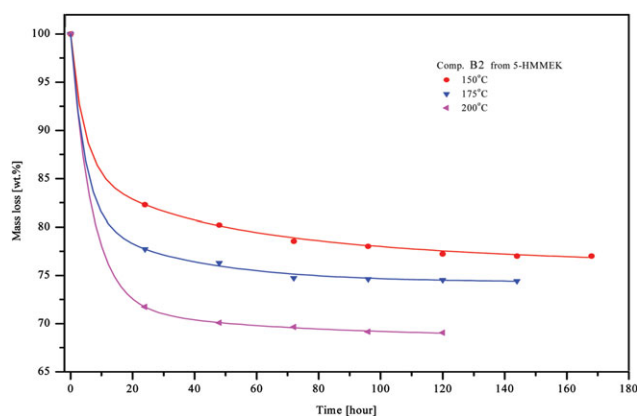
Figure 1. Thermal stability of foams obtained from melamine solutions in 5-HMMEK measured with mass loss at various temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
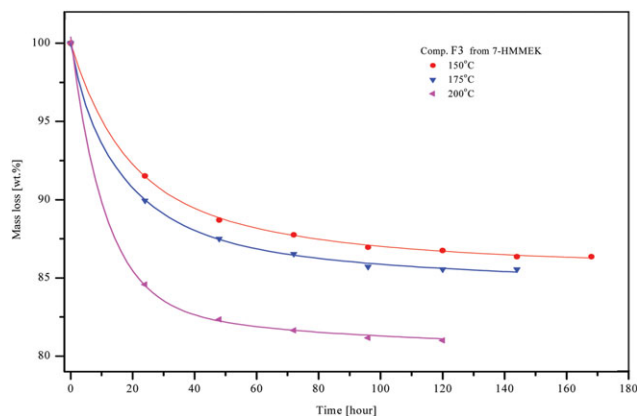
Figure 2. Thermal stability of foams obtained from melamine solutions in 7-HMMEK measured with mass loss at various temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
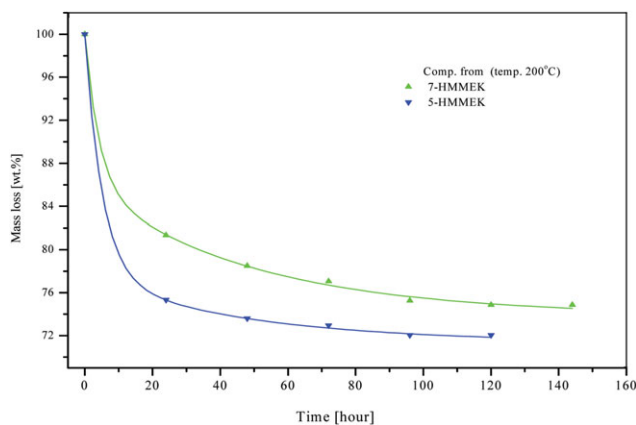
Figure 3. Thermal stability of foams obtained from melamine solutions in 5-HMMEK and 7-HMMEK measured with mass loss at temperature 200°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Values of compression strength of foams by exposure temperature and RS type are shown in Table III and in Figures 5 and 6. Increase in compression strength was observed in all compositions subjected to thermal exposure. In the case of foams obtained from melamine solutions in 5-HMMEK, compression strength is usually the highest after exposure to temperature 175 or 200°C (Figure 5), whereas in the case of foams obtained from melamine solutions in 7-HMMEK, the temperature of exposure had varied effect to increase in compression strength (Figure 6). It was observed that foamed melamine materials obtained from 5-HMMEK feature higher compression strength than those obtained from 7-HMMEK (Table III).

The Thermal Conductivity

The thermal conductivity of selected foams was measured, and the thermal conductivity coefficient was found to amount to 0.0481–0.0483 W m^{-1} K [the volume heat capacity: 0.0413–0.0427·10^6 (J m^{-3} K)]. For classical insulation by polyurethane foam, this coefficient amounts to 0.029–0.045 W m^{-1} K.

The Flammability of Foams

Knowledge of foamed materials behavior in fire is of great significance when considering their application. Flammability tests of porous melamine materials determined that all foams produced are self-extinguishing, and that they emit low amounts of smoke when in fire. It results from a well-known fact that melamine is an effective flame retardant.

Foams obtained from Mel-F-MEK resins extinguish more slowly than those obtained from Mel-F-CH resins.[6] It was also determined that materials with higher melamine content burn shorter than materials with higher melamine content.

In the case of selected foams, the speed of flame propagation on surface was examined. To that effect, they were exposed to open flame and time between foam ignition and reaching by flame of indicated line was measured. It was found that in the case of foams obtained from solutions of melamine in the 5-HMMEK and 7-HMMEK, the designated point is slowly reached by the flame if material contains a greater amount of melamine. The
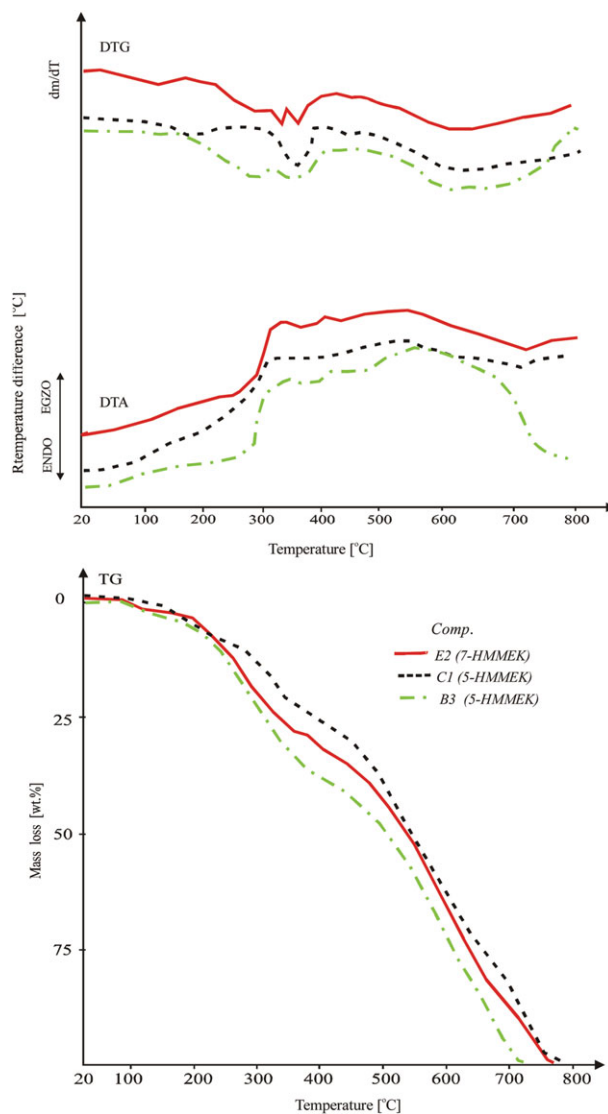
Figure 4. The differential thermal analysis (DTA) and thermogravimetry (TG) thermograms of selected foamed materials obtained from melamine solution in 5-HMMEK and 7-HMMEK. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
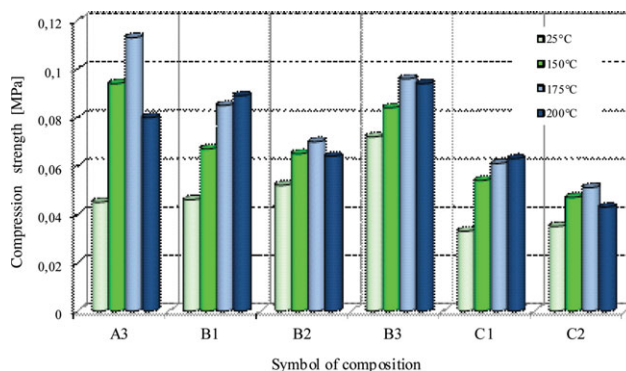
Figure 5. Compression strength of foams obtained from melamine solution in 5-HMMEK. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
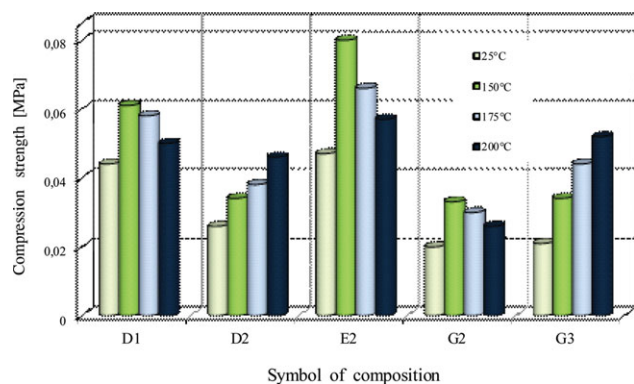
Figure 6. Compression strength of foams obtained from melamine solution in 7-HMMEK. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

presence of the maximum amount of melamine gives a result of $7-12$ mms^{-1}, and therefore, the more amount of melamine in the foam, the lower the rate of flame spread.

Properties of obtained foamed melamine materials (polyurethane foams) are better than of those obtained from cyanuric acid[8] and at the same time similar to properties of traditional polyurethane foams although foamed melamine materials are much superior in terms of thermal strength. Their advantage is improved mechanical strength after heating.

The resulting product is self-extinguishing foam, which is also an important advantage in comparison to the most commonly used foams. Melamine foams can be used as nonflammable thermal insulation, which can be applied up to temperature of 200°C. The following parts of the cycle describe possibilities for use of reactive solvents in production of oligoetherols with s-triazine ring.

CONCLUSIONS

1. By foaming the anhydrous melamine solutions in reactive solvents based on MEK using MDI, the melamine foam

materials were obtained with the density of less than 37.5 kgm^{-3}.

2. In comparison to conventional polyurethane foams, melamine foams are characterized by increased thermal stability (up to 200°C), measured by mass loss during heating and increase in compressive strength after thermal exposure, greater dimensional stability, and lower water absorption.

3. The polyurethane foams from melamine solutions in reactive solvents are self-extinguishing, which distinguishes them from conventional polyurethane foams and considerably extends the possibility of their application.

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