

Rigid Polyurethane Foams Modified with Selected Layered Silicate Nanofillers

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ABSTRACT: The aim of this study was to investigate the effect of three different nanofillers on the properties of rigid polyurethane foams, which were prepared by a one-step, laboratory-scale method from a two-component system at the ratio of NCO groups to OH groups equaled to 2. The reaction mixture consisted of the proper amounts of the commercial oligoether polyol, catalysts, water, nanoclays, and polymeric diphenylmethane diisocyanate. Three types of montmorillonite were used as clay component, i.e., montmorillonite modified by methyl tallow bis-2-hydroxyethyl ammonium (Cloisite[®]30B), a synthetic layered silicate (Laponite[®]RD), and an aluminium phyllosilicate absorbent, essentially impure clay consisting mostly of montmorillonite (Bentonite). Thermal properties of rigid polyurethane foams and nanocomposite foams were investigated by dynamical thermal analysis, thermogravimetry, oxygen index, and thermal conductivity measurements. It has been shown that the foams modified by selected nanofillers are characterized by high mechanical strength, as well as improved fire barrier properties. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2272–2281, 2013

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INTRODUCTION

In recent years, a steady increase in the production of polyurethane materials, which in 80% consist of polyurethane foams (PUFs), has been observed. Polyurethane foams are generated via mixing, foaming and cross-linking of mixtures of polyols and di- or tri-isocyanates with blowing agents and activators. PUFs have a highly significant place among synthetic materials. They are widely used in a rigid, elastic, or integral form, depending on the foam composition, component mass ratios, and processing conditions. Polyurethane foams are characterized by good mechanical strength, vibration-reducing properties, particular resistance to weathering, and resistance to organic solvents and oils. Different types of these foams have found application in many branches of industry such as, construction, furniture production, automotive production, clothing manufacturing, and aviation.¹

Rigid polyurethane (PUR) foams have a low coefficient of thermal conductivity (λ), which varies from 0.018 to 0.028 W m⁻¹ K⁻¹. Therefore, they could successfully replace currently used polystyrene insulating materials, which have the two-fold higher thermal conductivity, ranging from 0.030 to 0.048 W m⁻¹ K⁻¹.²

At present, a majority of studies are dedicated to improving the thermal insulation properties of porous materials and, at the same time, retaining their good mechanical characteristics.

In accordance with the Montreal Protocol on Substances that Deplete the Ozone Layer, the use of Freon, which in the past was commonly used as a blowing agent in the production of PUFs, has been banned.⁴ Due to the ban on Freon, hydrocarbons with low boiling points such as, pentane and isopentane are presently used as blowing agents. Both aforementioned compounds do not deplete the ozone layer however they are flammable and might be a fire hazard. It is possible to use water as a blowing agent in the PUFs production but the rigid urea groups, resulting from the reaction of isocyanate with water, worsen the mechanical properties of the foam.⁵

In order to increase PUFs resistance to burning, flammability-reducing antipyrenes (mostly chlorine and phosphorus containing derivatives) are added to the polyol mixture. Such modification however worsens the mechanical properties of the final product in a significant way.

In recent years, there has been increasing interest in modifying the properties of PUFs by using nanofillers, mainly

aluminosilicates.^{6–11} The results of numerous studies have shown that the introduction of nanofillers based on layered aluminosilicates into a polymer system resulted in the improvement of many properties compared to traditional polymers. The selection of proper components can result in achieving higher resistance to temperature, lower flammability,^{12–15} and improved mechanical strength¹⁶ and thermal stability.^{17–19} Composites filled with nanofillers are characterized by much better mechanical properties compared to composites containing traditional fillers. Moreover, nanocomposites display higher barrier properties. The improved fire resistance of organoclay nanocomposites is based on good distribution of lamellar structures inside the polymer. These structures prevent the penetration of external substances via the nanocomposite surface. Nanofillers limit to a large extent heat flow into the polymer. An improvement in thermal properties is caused by the reduced mobility of macromolecules, which form strong bonds with nanofillers.

The main aim of this study was to produce rigid polyurethane foams modified with selected fillers, characterized by improved flame resistance and better thermal and mechanical properties. Due to very good insulating properties, rigid polyurethane foams are mainly used in construction for thermal insulation of buildings. PUFs have low coefficient of thermal conductivity, better mechanical properties, and improved resistance to high temperatures than traditional polystyrene insulation. Despite all these advantages, polyurethane foams are rated as easy to ignite.³ Fire safety regulations define the requirements, which have to be fulfilled by insulating materials used in buildings. Therefore, the search for novel materials, which would decrease the flammability of rigid polyurethane foams, continues.

EXPERIMENTAL

Materials

Polyol. *Rokopol RF551* was used, which is a general purpose sorbitol based polyether polyol recommended for the production of rigid polyurethane foams. According to the manufacturer, the density of Rokopol RF551 at 25°C is 1.1 g cm⁻³; typical hydroxyl number is 400–440 mg KOH g⁻¹; viscosity (25°C) is 5.842 Pa·s; and the number average molecular weight is 600 g mol⁻¹ (PCC Rokita, Poland).

Surfactant. A silicon based surfactant *NIAX Silicone SR-393* was used (Momentive, Czech Republic).

Catalysts. Two catalysts, both purchased from Sigma-Aldrich, were applied, i.e., *K₁₂* (33% wt solution of potassium acetate in ethylene glycol) and *K Amin-2*-[2-(dimethylamino)ethoxy] ethanol.

Blowing agents. *n-Pentane Pure* (POCH, Poland) and distilled water were used as blowing agents.

Nanoclays. The following nanoclays were used: *Cloisite*[®] 30B, natural montmorillonite modified with a ternary ammonium salt; bulk density: 346 g L⁻¹; (Southern Clay Products); *Laponite*[®] RD, a synthetic layered silicate; bulk density: 1013 g L⁻¹; (Southern Clay Products); and *Bentonite*, an aluminium phyllosilicate absorbent, which is essentially impure clay,

consisting mostly of montmorillonite; bulk density: 1043 g L⁻¹; (ZEBIEC SA, Poland).

Isocyanate. *Izocyn B* (Chemical Plant Zachem), a polymeric diphenylmethane (4,4'-diisocyanate, pMDI) characterized by 31% of NCO groups, with the density of 1.22 g cm⁻³ at 25°C was used.

Preparation of Rigid Polyurethane Foams Modified by Nanoclays

Rigid polyurethane foams were produced by a laboratory-scale, single-step method from a two-component (A and B) system at the equivalent proportion of NCO and OH groups equaled to 2. In the first step, nanoclays were seasoned for 6 h at 100°C.

Component A (polyol mixture) consisted of proper amounts of oligoether, Rokopol RF 551, catalysts, chemical blowing agents, and nanoclay, the latter at 3, 6, and 9 wt %. It was prepared by vigorous stirring with a mechanical stirrer for 30 min, and by sonication with an ultrasonic homogenizer for 20 min. Next, nanoparticulated polyol matrix was mixed with the component B (polyisocyanate, pMDI), at a predetermined mass ratio, for 10 s at 3000 rpm. The resulting reaction mixture was poured into an open metal mold of approximate dimensions of 100 × 100 × 50 mm³. PUF samples after demolding were stored at 60°C for 24 h, and seasoned at the room temperature for another 24 h. The four systems were used to prepare 10 foam samples, as presented in Table I as follows.

System 1: Unmodified polyisocyanurate (PIR) PUR–PIR foam (numbered 1 in Table I)

System 2: PUR–PIR modified by nanoclay Cloisite 30B at 3, 6, and 9 wt % (numbered 2–4 in Table I).

System 3: PUR–PIR modified by nanoclay Laponite RD at 3, 6, and 9 wt % (numbered 5–7 in Table I).

System 4: PUR–PIR modified by nanoclay Bentonite at 3, 6, and 9 wt % (numbered 8–10 in Table I).

The sample code consists of an index referring to clay type and a number defining wt % of clay, for example: P₀ – unmodified PUR–PIR foam, P_{3%Clo} – foam with 3 wt % of Cloisite 30B, P_{6%RD} – foam with 6 wt % of Laponite RD, P_{3%Ben} – foam with 3 wt % of Bentonite.

Methods of Testing

After seasoning, the foams were cut and their properties were determined in accordance with the standards.

Foaming Properties. The following parameters were measured: the start time; the rise time, i.e., time when the foam reaches the maximum height; and the gelation time when a surface of the foam stops being tacky to the touch. The maximum reaction temperature was measured using a thermocouple which was placed in the reaction mixture. Temperature measurement was performed from the start to gelation time.

Physical Properties. Apparent density of PUF samples was calculated in accordance with PN-EN ISO 845:2000, as the ratio of the sample weight to the sample volume (g cm⁻³). Cube-shaped samples were measured with a slide caliper with an accuracy of 0.1 mm, and weighed using an electronic analytical balance with an accuracy of 0.0001 g.

Table I. The Composition of the Reaction Mixtures Used to Prepare PUR–PIR Foams with Variable Amounts of Cloisite 30B, Laponite RD, and Bentonite

Component Sample no.	System 1 (reference) content (%) PO	System 2 content (%)			System 3 content (%)			System 4 content (%)		
		P _{3%ClO}	P _{6%ClO}	P _{9%ClO}	P _{3%RD}	P _{6%RD}	P _{9%RD}	P _{3%Ben}	P _{6%Ben}	P _{9%Ben}
Rokopol RF551	15.3	14.9	14.3	13.9	14.9	14.3	13.9	14.9	14.3	13.9
NIAX Silicone SR-393	1.5	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
K ₁₂	0.7	0.7	0.7	0.6	0.7	0.7	0.6	0.7	0.7	0.6
K Amin	0.7	0.7	0.7	0.6	0.7	0.7	0.6	0.7	0.7	0.6
n-Pentane Pure	0.7	0.7	0.7	0.6	0.7	0.7	0.6	0.7	0.7	0.6
Water	1.6	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Cloisite 30B	-	3.0	6.0	9.0	-	-	-	-	-	-
Laponite RD	-	-	-	-	3.0	6.0	9.0	-	-	-
Bentonite	-	-	-	-	-	-	-	3.0	6.0	9.0
pMDI	79.5	77.2	74.7	72.4	77.2	74.7	72.4	77.2	74.7	72.4

Water absorption of PUF was characterized in accordance with PN-EN ISO 62:2008. Dried PUF disks (20 mm in diameter and 10 mm thick) were immersed in distilled water at room temperature for 24 h. Next, the samples were removed from the medium, blotted on a filter paper to remove excess water and weighed with an accuracy of 0.001 g.

Brittleness of PUF was determined in accordance with ASTM C-421-61; it was calculated as a percentage mass loss of 12 cubic samples (25 × 25 × 25 mm³) during a 10-min movement of the case. The measurement was performed in a wooden case with dimensions of 190 × 197 × 197 mm³, rotating at a speed of 60 rpm.

Thermal conductivity of PUR was measured with a Laser Comp Heat Flow Instrument (model Fox 200) according to ASTM C 518. A sample was placed in the test section between the two plates which were maintained at different temperatures during the test. The size of the specimen was 300 × 300 × 50 mm³.

Structure. X-ray diffraction (XRD) measurements were performed using a Bragg–Brentano X'PERT PHILIPS diffractometer equipped with a Cu anode X-ray tube and diffracted beam monochromator (40 kV, 30 mA, λ Cu $K\alpha$ = 0.1542 nm). PUF samples were scanned in an angle range from 1.5 to 10°.

The cellular morphologies of the foam samples in the direction of foaming were investigated with a *Delta Optical NJF-120A* metallographic microscope. Image analysis was performed on the obtained micrographs using ImageJ software. Feret's diameter is defined as the longest distance between any two points along the selection boundary, also known as maximum caliper.

Mechanical Properties. Compression strength of PUF samples was estimated in accordance with PN-EN ISO 604:2006 in parallel direction. Cube-shaped samples with dimensions of 50 × 50 × 50 mm³ were measured with a slide caliper with an accuracy of 0.1 mm. The compression test was performed on a Zwick/Roell tensile tester at a constant speed of 10 mm min⁻¹ until reaching 20% deformation.

Dynamical mechanical analysis (DMA) was performed by means of a Q800 DMA instrument (TA Instruments) apparatus with Single Cantilever holders according to the ASTM D4065 standard. Measurements were taken for samples of 40 × 10 × 4 mm³ for the temperature range from -80 to 250°C, at heating rate of 3°C min⁻¹ and frequency of 0.1 Hz.

Thermal Properties. In order to evaluate the thermal stability of PUFs, thermogravimetric analysis (TGA) was performed on 5-mg samples by means of a *NETZSCH TG 209* apparatus under argon atmosphere for the temperature range from 100 to 600°C and at a heating rate of 15°C min⁻¹.

Flammability. Flammability testing was performed according to the US standard UL 94 HB. The burning of a horizontal element made of synthetic material was conducted. Bar-shaped samples with dimensions of 127 × 12.7 × 10.7 mm³ were used. Marks were made on the surface of each bar at a distance of 25.4 and 101.6 mm from the end that is to be ignited.

Determinations of oxygen index were carried out under standard conditions in accordance with PN-EN ISO 45-2. Bar-shaped samples with dimensions of 100 × 10 × 10 mm³ were used. Prior to testing, samples were conditioned at 23°C for at least 88 h. Bars were placed inside the column of the oxygen index apparatus, and the minimum percentage of oxygen in the oxygen/nitrogen atmosphere, which marginally supported combustion, was measured. The flammability test result was reported as the arithmetic mean of five measurements.

The oxygen index value was calculated according to the following equation:

$$OI = \frac{O_2}{O_2 + N_2} \times 100 \quad (1)$$

where O_2 is the minimum oxygen concentration in the oxygen/nitrogen test atmosphere [cm³ s⁻¹], and N_2 is the nitrogen

Table II. Foaming and Physical Properties of the Foam Samples

Sample code	Foaming properties				Physical properties			
	Start time (s)	Growth time (s)	Gelation time (s)	Max. temperature of foaming process (°C)	Apparent density (kg m ⁻³)	Water absorption (%)	Brittleness (mass loss, %)	Thermal conductivity (mW mK ⁻¹)
P ₀	10	46	64	125.7	21.7 ± 2.0	85 ± 3	17 ± 2	26.1 ± 1.3
P _{3%Clo}	10	60	70	-	33.4 ± 3.0	50 ± 1	27 ± 3	21.1 ± 1.0
P _{6%Clo}	10	60	81	155.0	34.4 ± 4.0	89 ± 3	33 ± 2	26.3 ± 1.3
P _{9%Clo}	10	81	116	-	56.4 ± 5.0	123 ± 4	42 ± 4	38.4 ± 1.9
P _{3%RD}	13	61	123	-	32.4 ± 3.0	90 ± 5	10 ± 1	27.1 ± 1.4
P _{6%RD}	15	80	180	116.6	33.5 ± 3.1	78 ± 2	28 ± 2	26.2 ± 1.3
P _{9%RD}	15	130	390	-	32.6 ± 2.9	132 ± 4	60 ± 3	32.3 ± 1.6
P _{3%Ben}	13	68	123	-	25.4 ± 2.0	106 ± 3	33 ± 2	27.6 ± 1.4
P _{6%Ben}	14	73	180	89.8	23.9 ± 2.2	138 ± 4	25 ± 2	39.1 ± 2.0
P _{9%Ben}	15	121	256	-	22.8 ± 2.0	188 ± 5	35 ± 3	42.4 ± 2.1

content in the test atmosphere corresponding to the minimum oxygen concentration [cm³ s⁻¹].

The oxygen content was measured in a stepwise manner, with 0.5% intervals of oxygen concentration.

RESULTS AND DISCUSSION

The properties of all prepared polyurethane foams were assessed and presented in Tables II–IV.

Foaming and Physical Properties

The foaming time values increased with increasing amount of nanofiller, which could result from the relatively low activity of the catalysts used. The lowest foaming time values in modified PUR–PIR foams were observed in the case of System 2. The highest values of foaming time (start, growth, and gelation times) were observed in the samples containing 9 wt % of Laponite RD. The introduction of nanofillers inhibits the reactions. These results confirm the findings of Kim et al.²⁰ who demonstrated that the modification of rigid polyurethane foams with Cloisite 30B results in higher values of foaming time.

The reference polyurethane foam (i.e., System 1) was characterized by a very low apparent density (21.7 kg m⁻³) because the blowing agent used for its preparation contained 1.6% of water. Foams belonging to System 4 showed the smallest difference in density in relation to foam 1. The biggest density increase was observed in the case of foam modified with 9 wt % Cloisite 30B (56.4 kg m⁻³). This is caused by the smallest bulk density of nanofiller Cloisite 30B and consequently at 9 wt % of Cloisite 30B there was about three times more powder particles than in the case of Laponite or Bentonite. In other cases, the maximum density reached 34.4 kg m⁻³. The increase in apparent density in foams modified with nanofillers has been reported elsewhere.^{10,11,16,21,22}

The observed water absorption in comparison to the reference foam, foams belonging to System 4, was characterized by visibly increased water absorption. This was caused by the use of hydrophilic Bentonite. Other studies^{9,10} demonstrated that apart

from the formation of smaller cells, the use of nanofillers causes some defects in windows which, in consequence, results in the structure with a higher number of open cells.

Increased mass loss in samples modified with nanofillers, with an exception of sample P_{3%RD}, could be caused by more developed cell structure (i.e., higher number of small cells). Nanofiller molecules act as the precursors of cells which in microscale may be less resistant due to defects present on the molecule surface.

Thermal conductivity of PUR/clay nanocomposites was increasing for almost samples for all clays used in study. It can be caused by not uniformly clay dispersion in foam matrix, what also affected the cell structure increasing the number of large and open pores. In the case of foam P_{3% Clo} noted improvement the thermal conductivity was observed. This might be caused by better dispersion of this clay in the polyurethane matrix. This foam was also characterized by small cell structures.

The infuse of clay and different blowing agents on thermal conductivity was study by Kim et al.²³ The authors stated that the thermal conductivity of polyurethane foams strongly depends

Table III. The Average Values of Feret Diameter of the Foam Samples

Sample code	Feret diameter (μm)
P ₀	258 ± 62
P _{3%Clo}	210 ± 57
P _{6%Clo}	256 ± 59
P _{9%Clo}	455 ± 63
P _{3%RD}	297 ± 56
P _{6%RD}	296 ± 59
P _{9%RD}	353 ± 56
P _{3%Ben}	264 ± 32
P _{6%Ben}	291 ± 49
P _{9%Ben}	299 ± 40

Table IV. Mechanical and Thermal Properties of the Foam Samples

Sample code	Mechanical properties		Thermal properties					
	Compression strength (kPa) (Rs 10%)	Glass transition temperature (°C) T_g	Thermogravimetric analysis; foam mass reduction (%)			Flammability test UL 94HB		
			Temperature (°C)			Burning time (s)	Burning distance (mm)	Oxygen index (vol % O ₂)
5	10	50						
P ₀	97 ± 4.8	250	286	316	533	24.3	101.6	22.54
P _{3%Clo}	172 ± 8.6	260	302	328	480	16.9	34.2	23.45
P _{6%Clo}	170 ± 8.4	250	-	-	-	19.8	45.0	-
P _{9%Clo}	296 ± 12.2	210	319	343	574	40.9	34.1	24.10
P _{3%RD}	158 ± 7.9	250	300	318	410	20.6	101.6	22.05
P _{6%RD}	170 ± 7.6	230	-	-	-	31.4	101.6	-
P _{9%RD}	134 ± 5.4	220	287	306	448	26.7	101.6	21.69
P _{3%Ben}	86 ± 3.9	220	280	298	392	14.3	101.6	21.58
P _{6%Ben}	85 ± 4.7	220	-	-	-	11.8	101.6	-
P _{9%Ben}	98 ± 4.3	200	293	312	418	31.5	101.6	22.68

on thermal conductivity of blowing agent itself as well on the properties of additive, such as organoclay.

Structure

In Figure 1, the diffractograms of pure nanofiller and foam modified by adding 9 wt % of this particular nanofiller are presented.

Based on the analysis of X-ray diffractograms of nanofiller-modified foams, no diffraction maxima were detected for foams modified by Cloisite 30B and Laponite RD. This may indicate that the obtained samples are exfoliated nanocomposites with well-dispersed nanofiller. In the case of foams with Bentonite, there was a diffraction maximum. The Bentonite has a characteristic diffraction maximum at $2\theta = 6.8^\circ$ based on the Bragg's equation, corresponding to gallery spacing of 1.28 nm. The foam P_{9%Ben} shows characteristic diffraction peaks at $2\theta = 6.0^\circ$. The results indicated that the polyurethane molecules intercalated into the layers of the Bentonite forming the nanocomposites. Figure 2 presents the microstructure of pure PU foam and foams modified by addition of nanofillers Cloisite 30B, Laponite RD, and Bentonite at 3 wt %.

The distribution plots of Feret diameter of pure rigid PU foam and foams modified with nanoclays (i.e., Cloisite 30B, Laponite RD, and Bentonite), including the average values and standard deviations of the measured parameters, are shown in Table III and Figure 3.

Based on the microscopy images and the distribution of Feret diameter, it can be stated that the addition of 3 wt % of nanofiller Cloisite 30B resulted in more ordered structure, with a larger number of small (<300 μm) cells as compared to the reference foam. In the case of nanofiller Laponite RD, cells with larger diameters of 400–900 μm formed which may negatively influence the mechanical properties of the material displaying such disordered cellular structure. Modification of the polyurethane foam using Bentonite indicates nanocomposites with

homogenous structure. The average Feret's diameter increased with increasing amount of nanofiller. Only for addition of nanofiller Cloisite 30B in an amount of 3% reducing of cell size was observed, what could be explained by assuming that fillers, added in small amounts, act as nucleating agents reducing the cell size.

Mechanical and Thermal Properties

The results of measurements of compression strength, storage and loss modulus, and thermogravimetric are shown in Figures 4–7. Mechanical and thermal properties of the foam samples are collected in Table IV.

Figure 4 shows the compression strength–strain curves for pure foam and foams modified by addition of nanoclay Cloisite 30B, Laponite RD, and Bentonite at 3, 6, and 9 wt %.

System 2 and System 3 showed increased compression strength; it was improved by even a small amount of added nanofiller. The compression strength of the foams modified with Cloisite 30B and Laponite RD was higher than in the case of the not modified reference foam. The highest value of compression strength was observed for the foams modified by Cloisite 30B. The obtained results should be interpreted in terms of the differences in particle size and chemical structures of the nanoclays.²⁴ Foams modified by adding 9 wt % of Cloisite 30B were characterized by the highest value of compression strength, which had increased threefold that of the reference foam. On the other hand, the use of Bentonite for modifying rigid PUR–PIR foams did not affect their mechanical properties. The difference in effect was caused by the smaller bulk density of nanofiller Cloisite 30B. Basically, in the case of Cloisite 30B, there are more nanoparticles per 1 g of powder compared to Laponite RD and Bentonite. Moreover, the functional groups present in Cloisite 30B and Laponite RD can form chemical bonds with isocyanates, while in the case of clay Bentonite, only physical reinforcement is possible.

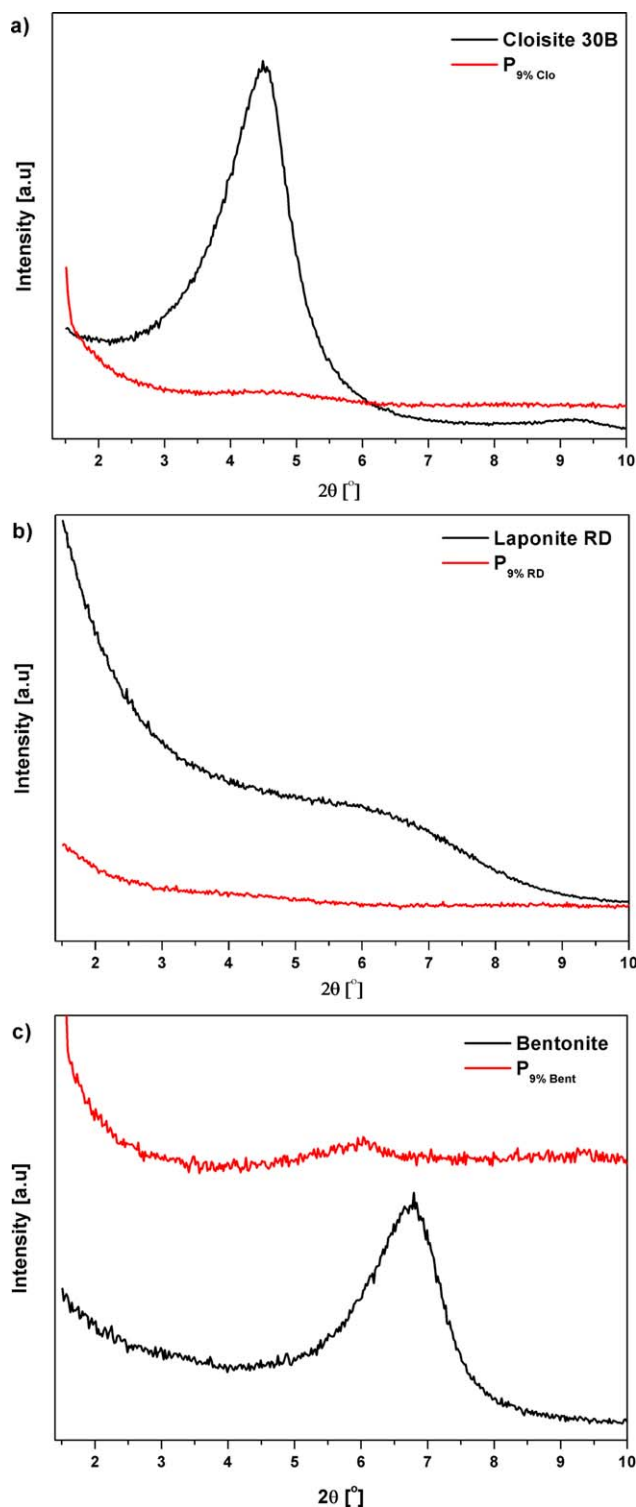


Figure 1. XRD patterns of pure nanoclays and foams modified by addition of (a) Cloisite 30B, (b) Laponite RD, and (c) Bentonite at 9 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It is well known that the dynamical mechanical properties of insulating materials are important, therefore the dynamical mechanical storage modulus (E') and dynamical mechanical loss

modulus (E'') of the obtained composites were examined in this study. Figure 5 shows the relationship between storage modulus (E') and temperature for rigid PU foams containing different percentages of used nanofillers.

In comparison to the reference foam, PU foams modified with nanofillers were characterized by increased storage modulus (E'). The highest E' values were observed for the samples modified with Cloisite 30B. This improvement was caused by the interactions between the nanofiller functional groups ($-\text{OH}$) and $-\text{NCO}$ groups of polymeric isocyanate (pMDI).⁸ The storage modulus values of foams containing Laponite RD or Bentonite were lower than E' for foam modified by Cloisite 30B. Lower values of the storage modulus were caused by bigger particle size and different chemical structure of these clays. The temperature dependence of loss moduli (E'') of reference foams and nanocomposite samples are shown in Figure 6. The E'' values of nanoclay-modified foams are higher than those of pure reference foam. It is because nanoparticles have a sheet-like structure, and when macromolecular chains move, large friction is generated between flat particles. That will subsequently result in higher E'' values. Our results on dynamical mechanical properties of polyurethane nanocomposite foams and the effect of modification with different types of nanoclay are similar to those reported by Xiong et al.²² and Nikje et al.²⁵

A lower T_g with higher clay content was reported by many investigators, for example Yasmin et al.²⁶ Another possible reason for the decrease in T_g could be the formation of an interphase between the silicate layers. What more, it can be formed due to plasticization of matrix by surfactant chains as suggested by Chen et al.²⁷ Other important factors that can affect T_g are the surface modification treatment, level of particle dispersion and the spacing between particles.

In Figure 7, the thermogravimetric (TG) and differential (DTG) curves for pure foam and foams modified by addition of nanoclay Cloisite 30B, Laponite RD, and Bentonite at 3 and 9 wt % are presented.

The temperature of 5% mass loss increased in the case of foams modified by addition of 3 and 9 wt % of nanofillers Cloisite 30B and Laponite RD. In the case of modification with clay Bentonite, only the addition of 9 wt % of nanofiller resulted in the increase of this temperature by 7°C. Foams modified by adding 9 wt % of Cloisite 30B were characterized by the highest thermal stability; 50% mass loss was recorded at 574°C. The use of Cloisite 30B improved the thermal resistance by 41°C. Nanofillers reduce the heat flow into a polymer due to good dispersion of layered silicates in the polymer matrix.

Flammability

In flammability test, the samples were extinguished when the flame passed the 101.6 mm marker. In the case of samples $P_{6\%RD}$, $P_{9\%RD}$, and $P_{9\%Ben}$, a decrease in burning rate was observed however the best thermal barrier was displayed by the foam modified with Cloisite 30B (System 2). The highest fire resistance values were obtained for nanocomposites with Cloisite 30B irrespective of the added amount of the nanofiller. These particular samples cease to burn before the flame reaches

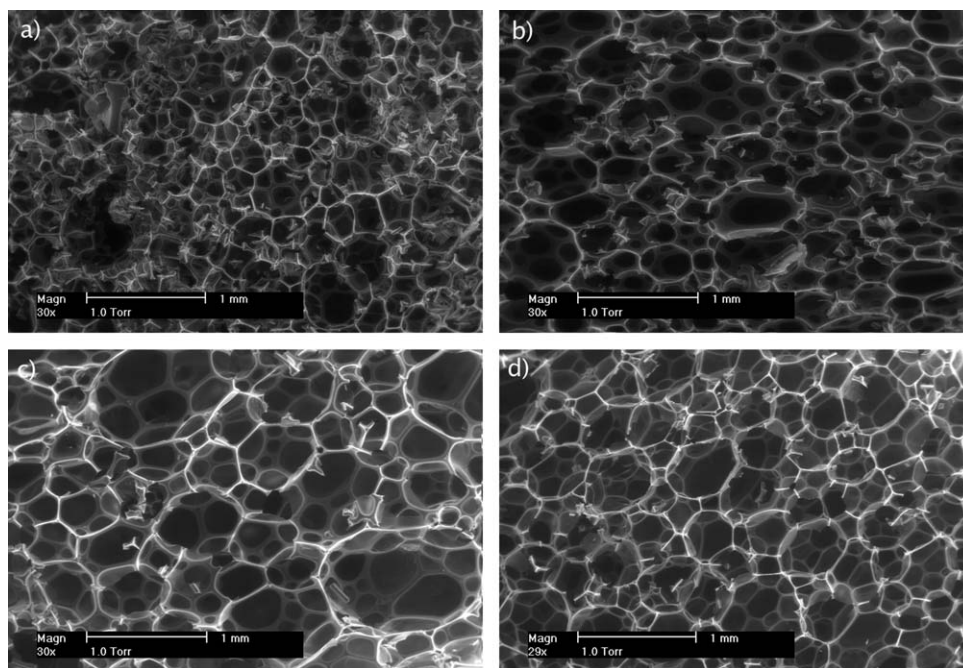


Figure 2. Microstructures of (a) pure rigid polyurethane foam and foams modified by addition of nanoclays (b) Cloisite 30B, (c) Laponite RD, and (d) Bentonite at 3 wt %.

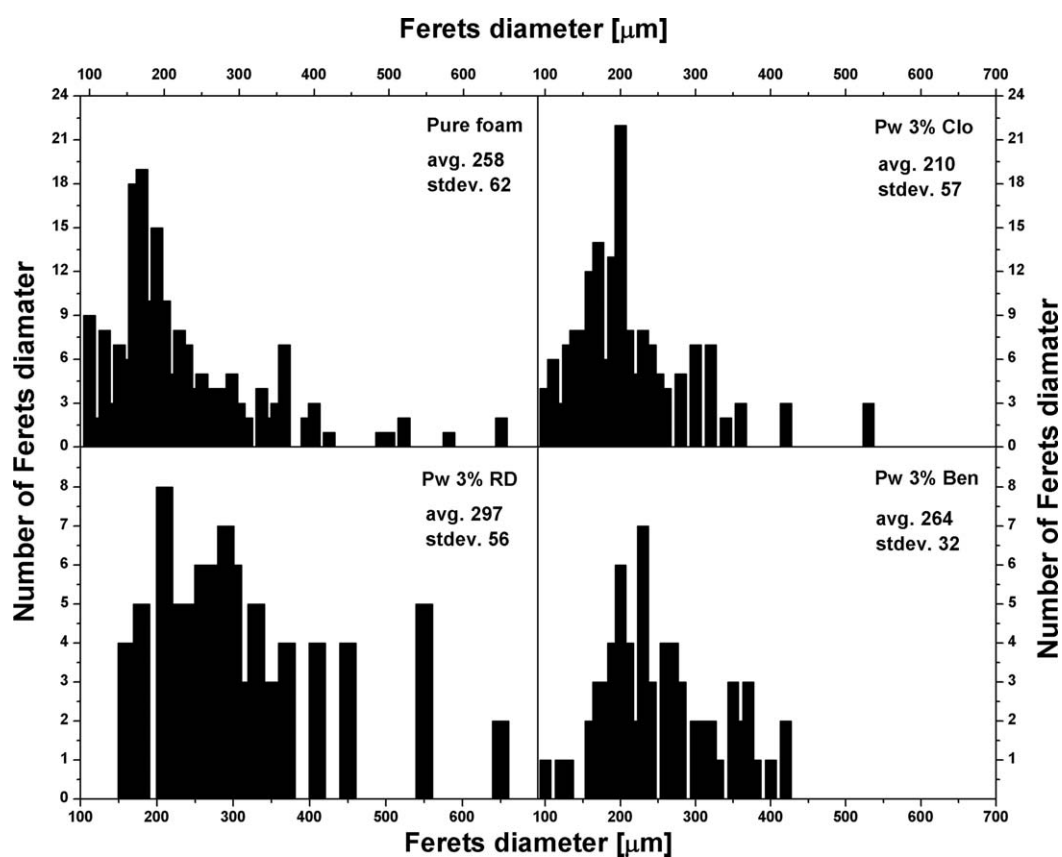


Figure 3. Effect of clays on the distribution of Feret diameter. The average values (avg) and standard deviations (stdev) of Feret diameter are given for each graph.

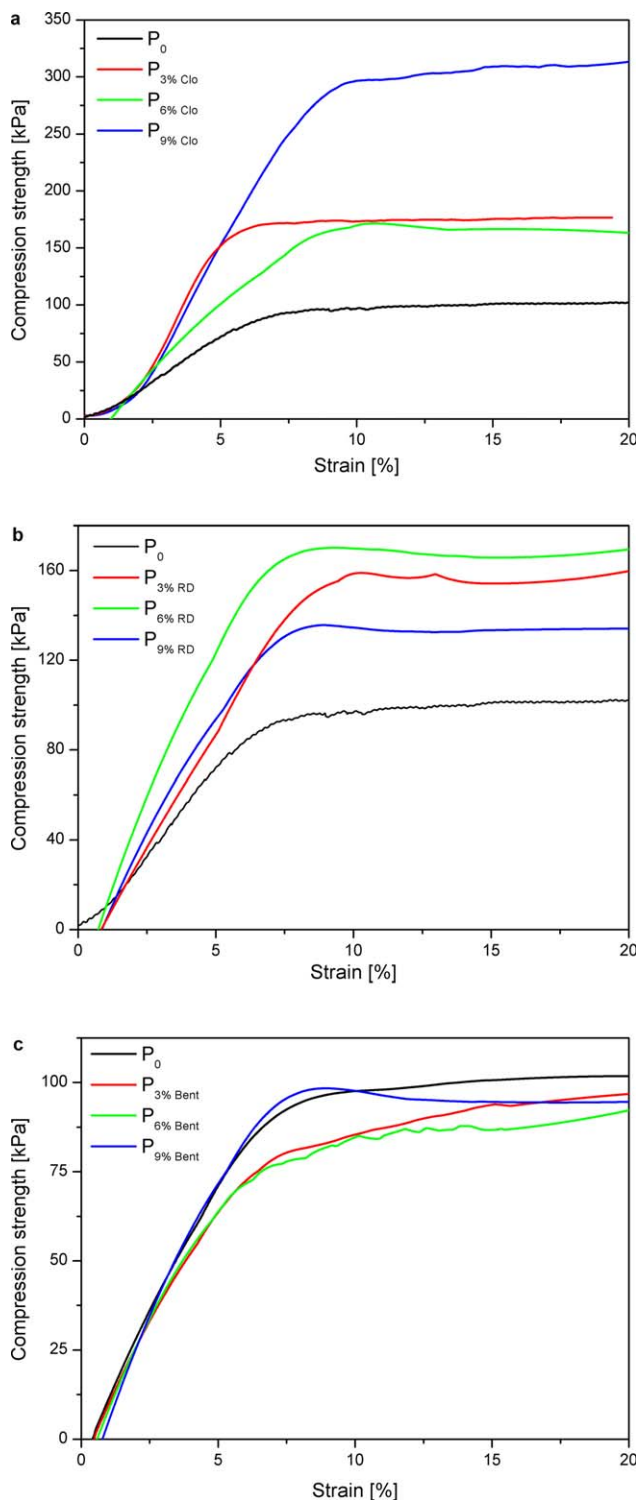


Figure 4. Compression strength–strain curves for pure foam and foams modified by addition of (a) Cloisite 30B, (b) Laponite RD, and (c) Bentonite at 3, 6, and 9 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

50 mm. The modification with Cloisite 30B resulted in charring of the sample; the charred area blocked flammable gases from penetrating deeper into the sample and therefore prevented further burning.

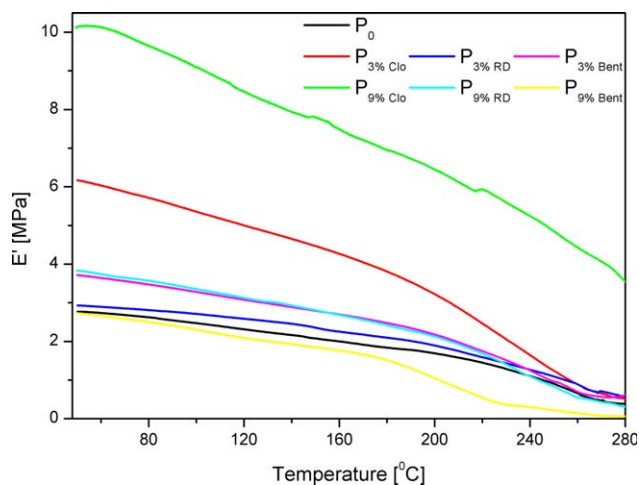


Figure 5. Temperature dependence of storage modulus of pure foam and nanocomposite foams with 3 and 9 wt % of nanofillers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The highest values of oxygen index of 23.45 and 24.10 were determined in foams modified by addition of Cloisite 30B at 3 and 9 wt %, respectively. In comparison to the reference foam (OI = 22.54), the other systems displayed lower oxygen index. One exception was sample P_{9%Bent}, with a much higher OI value of 22.68.

CONCLUSIONS

The aim of this study was to investigate the effect of three different nanofillers on the properties of rigid polyurethane foams. Foams were modified by adding 3, 6, and 9 wt % of a given nanofiller. It has been noted that even the lowest investigated 3 wt % amount of nanofiller affects the mechanical, thermal, and structural properties of the foams.

A modification with nanofillers is usually aimed at improving the mechanical properties of the final product.

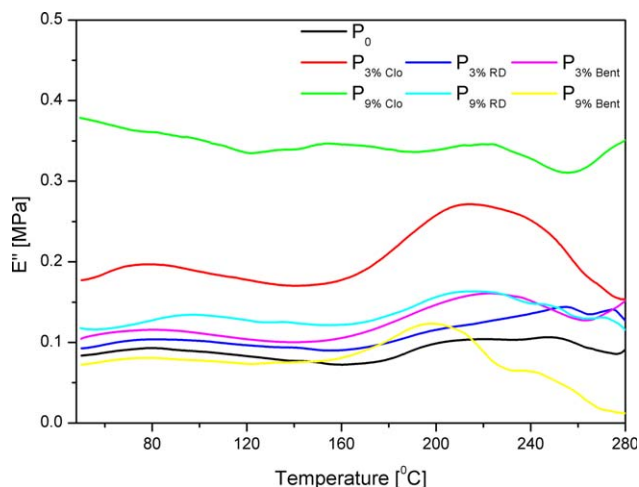


Figure 6. Loss modulus of pure reference foam and nanocomposite foams. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

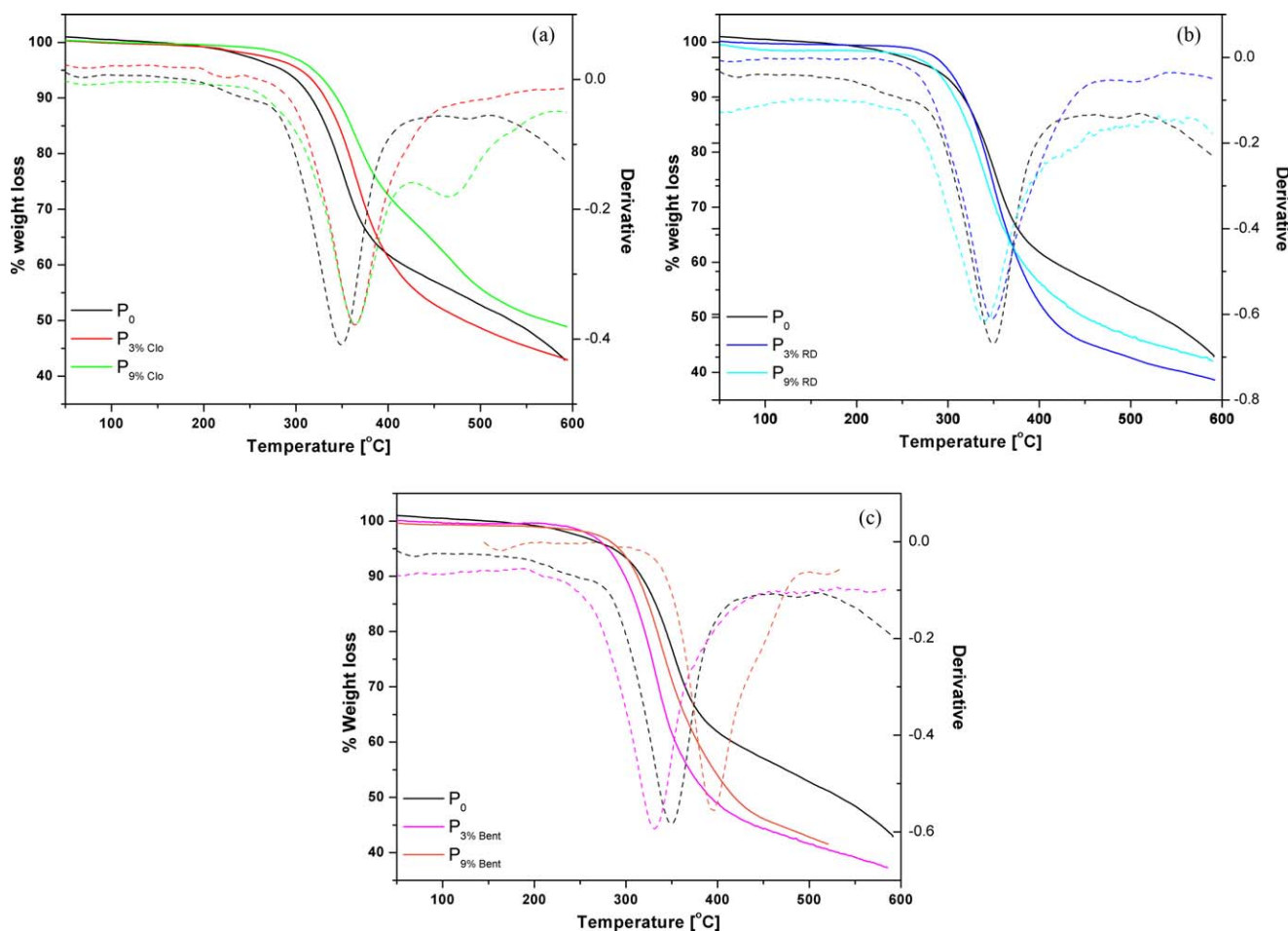


Figure 7. TG and DTG curves for pure reference foam and foams modified by adding (a) Cloisite 30B, (b) Laponite RD, and (c) Bentonite at 3, 6, and 9 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Among the three nanofillers used in this study, it was nanoclay Cloisite 30B which gave the modified foams (System 2) the best resistance to compression. Moreover, System 2 foams displayed the highest resistance to flames and high temperature. Flammability testing and the obtained oxygen index values indicate that nanoclay Cloisite 30B produces the highest barrier effect among the analyzed modifiers. The flammability testing produced valuable results, namely, the modification with nanofiller Cloisite 30B resulted in nanocomposite foams which in flammability test showed spontaneous extinguishing the flame.

In the case of foams modified with Laponite RD, the nanocomposites were characterized by similar parameters (apparent density, brittleness, compression strength, and thermogravimetric analysis) as nanocomposites from System 2, but only up to 6% filling, the greater amount of this nanofiller resulted in deterioration of the studied properties. This is caused by larger dimensions of the particle size in Laponite RD ($<250\ \mu\text{m}$) compared with nanofiller–Cloisite 30B ($<10\ \mu\text{m}$).

There are many types of fire retardant compounds however the application of fire retardants often results in worsened mechanical properties of the final product. This study demonstrated that by selecting appropriate components one can produce

materials which are more flame resistant and, at the same time, display improved mechanical properties. Depending on the type and amount of nanofillers used, parameters of the final product can be controlled. Despite the numerous publications on the subject of nanocomposites, it is still worth pursuing research in this field in order to discover the full range of modified polymers with unique and valuable properties.

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