Recent Advances on the Utilization of Nanoclays and Organophosphorus Compounds in Polyurethane Foams for Increasing Flame Retardancy

Javier C. Quagliano, Victor M. Wittemberg and Irma C. Gavilán García

Abstract Recent advances on fire retardants utilized in polyurethane foams were reviewed, mainly focusing on organophosphorus compounds. The application of nanotechnology for developing novel fire retarded nanocomposites is discussed as well, focusing in the addition of nanoclays to polyurethanes. The review is focused on flame retardants known or believed by the authors to be in actual use at the time of writing, without expanding on recent proprietary or patented information. Although fire retarded nanocomposite is an increasing area of research, still market utilization is to be developed.

1 Introduction

All organic polymers are combustible. They decompose when exposed to heat, decomposition products burn, smoke is generated, and the products of combustion are highly toxic, even if only CO and CO_2 [24]. The use of flame retardants to

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J. C. Quagliano (✉)
Organic Synthesis Division, Applied Chemistry Department, Instituto de Investigaciones Científicas y Técnicas para la Defensa (CITEDEF), Avenue Juan Bautista de Lasalle 4397
B1603ALO Buenos Aires, Argentina
e-mail: jquagliano@citedef.gob.ar

V. M. Wittemberg
Analytical Chemistry Division, Applied Chemistry Department, Instituto de Investigaciones Científicas y Técnicas para la Defensa (CITEDEF), Avenue Juan Bautista de Lasalle 4397
B1603ALO Buenos Aires, Argentina
e-mail: vwittemberg@citedef.gob.ar

I. C. Gavilán García
Faculty of Chemistry, National Autonomous University of Mexico (UNAM), Mexico, Mexico
e-mail: irmac@unam.mx

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reduce the flammability of polymers and production of smoke or toxic products during their combustion has become an important aspect of the research, development, and application of new materials. Among polymers, cellular materials like polyurethanes possess a high surface area per unit mass and this resulted in almost complete pyrolysis of combustible matter [20]. Polyurethanes, in the absence of flame retardants, are extremely combustible.

There are four main chemical groupings of flame retardants. These are inorganics (e.g. aluminum trioxide and magnesium hydroxide), nitrogen-based organic, organophosphorus (e.g. phosphate esters), and halogenated flame retardants [3]. Considering a broader range of applications as with plastics and textiles, fire retardants fall into several distinct classes (1) alumina trihydrate (2) halogenated compounds usually used in combination with antimony oxide (3) borax and boric acid and (4) the phosphorus nitrogen and phosphorus halogen compounds [25]. Respect to their reactivity with polymers, fire retardants are classified in reactive and additive. Polyurethane foam is one area where phosphorus flame retardants are often used due to their effectiveness [44].

Recently, nanotechnology has been described as the next great frontier of materials research because nanocomposite formation brings about improved material performance, including enhanced mechanical, thermal, optical, dimensional, and barrier performance properties [14]. This technology has also been developed for polyurethanes. Regarding fire retardancy, polyurethane nanocomposite preparation methods were reviewed, including characterization of the composites, thermal stability and combustion behaviour [9, 22, 43].

2 Fire Retardants in Polyurethanes

Because of the banning of pentabromodiphenyl ether (PBDE) in Europe and voluntary withdrawal of this product from the market in the US, the polyurethane (PU) industry is searching for a more environmentally acceptable low-scorch alternative. For polyurethane foams, the most commonly used flame retardants include chlorinated phosphate esters that provide cost-effective performance at a significant disadvantage in thermal resistance (scorch resistance) [26]. Also a mixture of an alkyl tetrabromobenzoate and a triaryl phosphate has been used commercially for the purpose of avoiding scorch. Both halogenated and halogen-free solutions are being considered but the PU industry now seems to have a preference for the halogen-free products, generally containing phosphorus [18]. Progress in flame retardancy of polyurethane and polyisocyanurate foams was also reviewed by Levchik and Weil [17, 19]. Major progress in the area of flame-retardant PUs in recent years is found in the field of phosphorus- or silicon-containing products, especially reactive ones. Inorganic additives remain of great interest, especially in PU-based intumescent coatings [40].

Organophosphorus compounds have a long history of use as fire retardant in polymers in general and particularly polyurethanes. Since the advent of polyvinyl chloride (PVC) in the 30, tricresyl phosphate was known as a fire retardant for this plastic. Later it was shown that the o-isomer is neurotoxic, and tricresyl phosphates made from *m,p*-cresol continued to be used. Several other alkyl phenyl and dialkyl phenyl phosphates were developed [41]. Many other organophosphorus fire retardants include halogens, such as halo alkyl phosphates. Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) or tris(chloroisopropyl) phosphate (TCPP) have been, and are currently, extensively used. This later has substantially reduced volatility and is more stable than TDCPP. There was some earlier use of tris(2,3-dibromo-1-propyl) phosphate but that compound was removed from the market when it was found to be mutagenic and carcinogenic. The chlorine analogs were found not to share that problem. Also, chlorinated alkyl phosphate, available as AMGARD V6 is utilized in polyurethanes. Tetrabromophthalic anhydride and its derivative diol are reactive flame retardants mainly used in polyurethanes. Also tribromoneopentyl alcohol is used as a reactive flame retardant for polyurethanes. Its high solubility in urethanes allows reaction of the single hydroxy functionality to form pendant urethane groups [26]. Generally phosphorus appears to act as an acid precursor in the solid phase to induce decomposition pathways that result in a reduced combustion and an increase in charring.

A huge amount of research was done in the last two decades to develop low-toxicity fire retardants for polyurethanes. Aromatic phosphates are another type of flame retardants which are currently used in polyurethane foam found in home furnishings. However, there is also the concern of exposure to aromatic phosphates [3].

The leading method for flame retarding rigid foam is to use additives, although reactive diols are occasionally employed where there is some special requirement. The leading additives are tris(2-chloroethyl) phosphate (now less used) and tris (1-chloro-2-propyl) phosphate [40]. Altogether, several types of fire retardants have been utilized in polyurethanes: both organic, as for example melamine [28], melamine polyphosphate and melamine cyanurate [26, 34] and inorganic, such as alumina trihydrate [27]; zinc borate [42]; zinc stearate (not used as a flame retardant but as a miscibility adjuvant) [23] and expanded graphite [13]. Among organics, organophosphorus compounds in polyurethanes, we found oligomer phosphates [1]; phosphonates like dimethyl methylphosphonate (DMMP) and oligomer phosphonates; phosphine oxides and other less common such as pyrophosphoric lactone as fire retardant coating [11] and 5,5,5′,5′,5″,5″-hexamethyltris (1,3,2,-dioxaphosphorinanemethan)amine 2,2′,2″-trioxide (XPM-1000 from Monsanto), advocated to be used in flame-retardant polyurethanes formulations [45]. Oligomeric cyclic phosphonates are utilized in rigid polyurethanes foams, and have been known since more than 50 years. They have excellent thermal and hydrolytic stability and are extensively used. On the other side, oligomeric chloroalkyl phosphonates such as Antiblaze 78 (Mobil) and Phosgards, once used in rigid PU foams, are not utilized in the market because of environmental and toxicological reasons [36]. Phosphazenes, both cyclic and polymeric, have been examined for their application as flame-retardant materials. A blend of poly [bis(carboxylatophenoxy)-phosphazene] with polyurethane precursors resulted in a urethane foam which exhibited increased thermal stability relative to the pure polyurethane [2]. An aromatic-substituted cyclic phosphazene, 2,4,6-triphenoxy-2,4,6-tri-(hydyoxyethoxy) cyclotriphosphazene (TPTHCP) was synthesized and used as a flame retardant to improve the flame retardancy of PU foams. Self extinguishing foam could be obtained when the phosphorus content was 1.5–2.0 wt% [10]. However, they are not utilized in practical applications. Sivriev et al. [31] synthesized a phosphorus- and nitrogen-containing polyol by condensation of tetrakis(hydroxymethyl)phosphonium chloride with diethanolamine. The effects of the structure and the content of the phosphorus- and nitrogen-containing polyol on properties of the polyurethanes, especially resistance to combustion, have been investigated. They demonstrated that the new phosphorus and nitrogen-containing polyol is an efficient flame retardant for rigid polyurethane foams. However, more recent research on these materials was not continued. There is abundant literature in this area regarding fire retardancy, and utilization is driven by a balance of cost and performance.

Phosphine oxides have been found highly effective in polypropylene [38]. Research on these compounds has continued. A phosphorus and nitrogen-containing polyol has been synthesized by condensation of tetrakis(hydroxymethyl) phosphonium chloride with diethanolamine. The newly synthesized polyol-tris[N,N-bis-(2-hydroxyethyl)aminomethyl] phosphine oxide (TPO) has been used in the preparation of rigid polyurethane foams with reduced flammability [31]. Phosphine oxides are expensive and this significantly limits their application [26].

It was shown early in fire retardant development that for a given series of related structures, either aliphatic or aromatic, the phosphates and phosphonates were superior to the phosphites (which are often hydrolytically sensitive) [6]. Novel organophosphorus fire retardant methyl-DOPO: 9,10-dihydro-9-oxa-methylphosphaphenthrene-10-oxide, which is a phosphinate, was considered for flexible polyurethane foam although more usually used in epoxy laminates. At temperatures where urethanes depolymerize, methyl-DOPO releases low molecular weight species like HPO, CH_3PO, or PO_2. These species are able to scavenge the H- and OH-radicals in the radical chain reactions of the flame [16].

Some researchers synthesized inherent flame retardant polyurethanes containing phosphorus that can react with isocyanate. Phosphorus-containing polyurethanes were synthesized by the reaction of phosphorus-containing diisocyanates and diols. Some newer phosphorus containing polyurethanes have highly flame retardant properties; the LOI values of these polyurethanes are around 29–33 [10]. A phosphorus- and nitrogen-containing polyol [polyol-bis(hydroxymethyl)-*N*,*N*-bis(2-hydroxyethyl) aminomethylphosphine oxide, AMPO] was used in the preparation of rigid polyurethane foams and were compared to polyurethane foams prepared on the basis of the commercially available flame retardant diethyl-*N*,*N*-bis(2-hydroxyethyl)aminomethylphosphonate (Fyrol 6). The polyurethane foams with AMPO exhibit a slight increase in the resistance to combustion (oxygen index) and a noticeable improvement in the thermal and mechanical properties [30].

The influence of several fire retardants on compressive strength and fire behaviour of rigid polyurethane foams was studied with ammonium polyphosphate, melamine cyanurate, alumina trihydrate, borax, and expanded graphite. In general, the cell size decreased, and compressive strength increased, as filler percentage was increased. One exception to this trend was borax, which led to a significant loss in compression strength of PU when it was added at the 15 % level [5].

3 Polymer-Layered Silicate Polyurethane Nanocomposites

Polymer-layered silicate nanocomposites are a new type of material, based on smectite clays usually rendered hydrophobic through ionic exchange of the sodium interlayer cation with an onium cation. They may be prepared via various synthetic routes comprising exfoliation adsorption, in situ intercalative polymerization and melt intercalation [12].

The use of nanoclays in polymers to impart fire retardancy to polyurethanes has been subject to numerous investigations, including preparation, properties and uses of this new class of materials. Nanoclays are interesting materials that are nanometric in only one dimension: they are formed by sheets of few nanometeres thick to hundred thousands nanometers long. There are many investigations about the use of clays both alone or with other compounds to flame retard polyurethanes. These compounds usually contain phosphorus, nitrogen or both, and are added to the polyol component of PU. Although the increasing research on nanocomposites for its fire retardant properties, very often polymer nanocomposites exhibit low flammability in terms of peak of heat release but fail other tests such as UL-94 rating and limiting oxygen index (LOI). This can be overcome combining nanoparticles with conventional fire retardants [7].

Wang and Pinnavaia [37] have synthesized intercalated nanocomposites based on elastomeric PUs. They used an organomontmorrillonite modified with dodecylamine or octadecylamine swollen in a polyol and then cross-linked with an isocyanate prepolymer. PU elastomeric matrices exhibit a sizeable increase in tensile stress at break upon the addition of small quantities of nanofillers. Processing, structure and properties of polyurethane/clay nanocomposites were studied by Cao and coworkers [8]. They found that the morphology and properties of PU nanocomposites and foams greatly depend on the functional groups of the organic modifiers, synthesis procedure and molecular weight of the polyols because of the chemical reactions and physical interactions involved. A novel intumescent flame retardant, namely montmorillonite (MMT) modified with a compound containing phosphorus–nitrogen structure (called c-MMT), was prepared by ion exchanging of the nanometer Na-montmorillonite (Na-MMT) with a phosphorus-nitrogen compound. The results showed that the addition of flame retardant c-MMT enhanced the thermal stability and flame retardancy of polyurethanes significantly. The authors concluded that exfoliated montmorillonite incorporated into polyurethane systems by in situ polymerization enhanced the thermal stability and flame retardancy of PU significantly [15]. Also, the nanoscale morphology of segmented polyurethane (SPU) nanocomposites containing various proportions of organomodified montmorillonite (MMT) was reported [21]. Nanoparticles such as organoclay MMT and carbon nanotubes in thermoplastic PU were reported to act mainly in a physical way (no chemical interactions) reinforcing intumescent char [7]. Mechanical properties of nanoclay-PU composites were studied. Data obtained from the compressive stress–strain curves revealed that the strength and modulus of polyurethane foam increase by addition of organoclay up to 1 wt% and then decrease [35]. Thirumala et al. [33] found that the compressive strength of organoclay/organically modified nanoclay (OMC) filled PU foam (PUF) increased up to 3 parts per hundred of polyol (php) by weight of OMC loading and then decreased. Dynamic rheological studies were performed on thermoplastic PU (TPU) with the incorporation of organoclay, showing increased dynamic viscosity and storage modulus, which was attributed to the formation of an interphase between soft and hard segments of the TPU matrix and effective dispersion of the organoclay [4].

Incorporation of commercial and laboratory-prepared nanoclays in a TDI-based polyurethane was done in our laboratory. Organically-modified clays interchanged with cetyl trimethyl ammonium bromide (CTAB) were incorporated in the polyol component of the PU at a high shear mixing rate (in situ intercalative polymerization), resulting in an exfoliated clay, which is nanometric in one dimension. This nanoclay, when dispersed in the polyurethane, resulted in the same fire retardancy rating (UL-94) than when the polyurethane was treated with a commercial nanoclay [29]. These results are in agreement with those obtained by Huang et al. [15].

The influence of surface-modified nanoclay on the self-organized nanostructure of segmented polyurethane composites was investigated [21]. Local researchers have studied the mechanical properties of montmorillonite-filled polyurethane foams and found an enhancement in the mechanical properties for the PUF sample at 5 wt% of MMT [32].

4 Commercial Applications

Despite the huge amount of literature existent in this field, which we have only reviewed in a condensed way, it is important to stress that fire retardant additives should not jeopardize polyurethane performance in general uses. The choice of suitable polymeric flame-retardants has to be restricted to species that allow retention of the advantageous mechanical properties of the polyurethane. Commercial applications were thoroughly reviewed by Levchik and Weil [18]. Tris(2-chloroisopropyl) phosphate and tris(dichloroisopropyl) phosphate are adequately stable in many formulations and have been used widely in polyurethanes. A non-halogenated phosphorus additive, which has had usage in rigid polyurethane foam for a long time, is dimethyl methylphosphonate (DMMP). It contains 25 wt% phosphorus (near the maximum possible for a phosphorus ester) and it is therefore highly efficient on a weight basis as a flame retardant. Triaryl phosphates, specifically triphenyl phosphate, isopropylphenyl diphenyl phosphate, tricresyl phosphate and trixylenyl phosphate all find some use in rigid foam formulations. Although reactive phosphorus- or halogen-containing fire retardants are on the market, it is believed that the use of additives is dominant in both rigid and flexible polyurethanes. From an environmental point of view, the reactive or reacted-in flame retardant has less likely to become an air and water pollutant in contrast with additive flame retardants. A good compromise is an oligomeric additive that has no vapor pressure or water-solubility, thus also meeting the environmental requirements.

Among reactive fire retardants, the Exolit OP 5xx series for polyurethanes in manufactured by Clariant. They are reactive flame retardants which integrate into the polyurethane matrix like a polyol. They show no migration, are more effective than the usual additive flame retardants and have only a minimal impact on the material properties. The three largest markets are transportation, furniture and carpet backing. Carpet backing uses mostly alumina trihydrate (ATH) as the flame-retardant additive, the other markets use an ever-increasing variety of approaches. A major fraction of the flexible polyurethane foams used in furniture is flame retarded. Additives are the dominant means, although much research has been expended on reactives.

When slightly volatile additives such as tris(1,3-dichloro-2-propyl) phosphate are used as flame retardants in automobile seating foams, there is often a detectable fogging of the inside of the windshield if the passenger compartment of the vehicle is warm. Other components of the foam, such as the catalysts and surfactants can also contribute to the fogging. There are various industry tests for windshield fogging. Where the monophosphate fails this test, it is usual to use diphosphates or oligomeric phosphates or phosphonates. The most widely used non-fogging flame retardant is tetrakis(2-chloroethyl) 2, 2-bis(chloromethyl)-1,3-propanediyl diphosphate.

The commercial development of several phosphorus-containing diols occurred in response to the need to flame-retard rigid urethane foams used for insulation in the transportation and construction industry. The earliest produced was a diol obtained from propylene oxide and dibutyl acid pyrophosphate [38]. A commercially significant phosphorus diol is diethyl bis(2-hydroxyethyl)aminomethylphosphonate (a trade mark for this chemical is Fyrol 6), especially useful in spray foams. It is synthesized by reaction of diethanolamine, formaldehyde and diethyl phosphite. It is stable in polyol-catalyst mixtures and imparts humid-aging resistance to foams. This is a reactive flame retardant, as the diol structure permits permanent incorporation of the phosphonate group into the urethane foam. The phosphonate linkage is on a side chain rather than in the backbone of the polyurethane, which increases the hydrolytic stability [39]. Most recent non-halogenated polyols containing phosphorus are utilized, as Clariant's hydroxy-terminated ethyl phosphate oligomer, as well as brominated diols.

5 Conclusions

Organophosphorus flame retardants are in an active state of development driven by their good performance and also by environmental and regulatory problems with the brominated flame retardants. Literature sources were mostly taken from the publications from the last decade, with reference to previous ground older publications. Nanoclay incorporation into polyurethane foams for increasing flame retardancy appears to be a new area for development of commercial future products, the same as with other industrial polymers. Current publications show that nanoclays exert improved flame retardant properties mainly when acting synergistically with conventional fire retardants.

References

1. Aaronson, A., Bright, D.: Oligomeric phosphate esters as flame retardants. Phosphorus, Sulfur, and Silicon and the Related Elements **109**, 83–86 1,4 (1996)
2. Allcock, H.: Chemistry and applications of polyphosphazenes. Wiley, New York (2003)
3. Andrae, N.: Durable and environmentally friendly flame retardants for synthetics. North Carolina State University, 2007. Cited: U.S. Consumer Product Safety Commission (CPSC) Staff. In Nomination of FR Chemicals for NTP Testing (2007)
4. Barick, A.K., Tripathy, D.K.: Effect of organically modified layered silicate nanoclay on the dynamic viscoelastic properties of thermoplastic polyurethane nanocomposites. 8th International Conference on Composite Science and Technology, ICCST8, Kuala Lumpur (2011)
5. Barikani, M., Askari, F., Barmar, M.: A comparison of the effect of different flame retardants on the compressive strength and fire behaviour of rigid polyurethane foams. Cell. Polym. **29**(6), 343–358 (2010)
6. Batorewicz, W., Hughes, K.: Some structure—activity correlations for halogen and phosphorus flame retardants in rigid urethane foam. Fire Retardants, International Symposium on Flammability and Fire Retardants, Proceedings, Cornwall, 1 May 1974 through 2 May 1974 (1974)
7. Bourbigot, S., Samyn, F., Turf, T., Duquesne, S.: Nanomorphology and reaction to fire of polyurethane and polyamide nanocomposites containing flame retardants. Polym. Degrad. Stab. **95**(3), 320–326 (2010)
8. Cao, X., Lee, J., Widya, T., Mocosko, C.: Polyurethane/clay nanocomposites foams: processing, structure and properties. Polymer **46**, 775–783 (2005)
9. Chattopadhyay, D., Webster, D.: Thermal stability and flame retardancy of polyurethanes. Prog. Polym. Sci. **34**, 1068–1133 (2009)
10. Chen, L., Wang, Y.: A review on flame retardant technology in China. Part I: development of flame retardants. Polym. Adv. Technol. **21**, 1–26 (2010)
11. Choi Y.: Synthesis of phosphorus-containing two-component polyurethane coatings and evaluation of their flame retardancy fire and polymers, Chap. 9, pp. 110–122. ACS Symposium Series, vol. 797, Washington DC (2001)
12. Dubois, P., Alexandre, M.: Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Mater. Sci. Eng. **28**, 1–63 (2000)
13. Duquesne, S., Le Bras, M., Bourbigot, S., Delobel, R., Vezin, H., Camino, G., Eling, B., Lindsay, C., Roels, T.: Expandable graphite: a fire retardant additive for polyurethane coatings. Fire Mater. **27**(3), 103–117 (2003)

14. Hu, Y., Song, L.: Nanocomposites with halogen and non intumescent phophorus flame retardant additives. In: Morgan, A.B., Wilkie, C.A. (eds.) Flame Retardant Polymer Nanocomposites. Wiley, New York (2007)
15. Huang, G., Jao, J., Li, Y., Han, L., Wang, X.: Functionalizing nano-montmorillonites by modification with intumescent flame retardant: preparation and application in polyurethane. Polym. Degrad. Stab. **95**, 245–253 (2010)
16. König, A., Kroke, E.: Methyl-DOPO-a new flame retardant for flexible polyurethane foam. Polym. Adv. Technol. **22**(1), 5–13 (2011)
17. Levchik, S., Weil, E.: Thermal decomposition, combustion and fire-retardancy of polyurethanes—a review of the recent literature. Polym. Int. **53**(11), 1585–1610 (2004)
18. Levchik, S., Weil, E.: A review of recent progress in phosphorus-based flame retardants. J. Fire Sci. **24**(5), 345–364 (2006)
19. Levchik, S., Weil, E.: Recent progress in flame retardancy of polyurethane and polyisocyanurate foams. Fire and Polymers IV, Chap. 22, pp. 280–290. ACS Symposium Series, vol. 922 (2006)
20. Modesti, M., Lorenzetti, A.: FR design for foam materials. In: Wilkie, A.C., Morgan, A.B. (eds.) Fire Retardancy of Polymeric Materials, 2nd edn, pp. 763–781. CRC Press, Boca Raton (2009)
21. Mondal, M., Chattopadhyay, P., Setua, D., Chas, N., Chattopadhyay, S.: Influence of surface-modified nanoclay on the self-organized nanostructure of segmented polyurethane composites. J. Fire Sci. **24**(5), 345–364 (2006)
22. Mouritz, A., Gibson, A.: Fire properties of polymer composite materials. Solid Mechanics and its Applications. Chapter 2. Thermal Decomposition of Composites on Fire. Springer, New York
23. Najafi-Mohajeri, N., Jayakody, C., Nelson, C.G.: Calorimetric analysis of modified polyurethane elastomers and foams with flame-retardant additives fire and polymers, Chap. 7, pp. 79–89. ACS Symposium Series, vol. 797 (2001)
24. Nelson, G. L., Wilkie, C. A.: Fire Retardancy in 2001, Chap. 1, pp. 1–6. Fire and Polymers—ACS Symposium Series, vol. 797 (2001)
25. NPCS Board of Consultants & Engineers: Handbook on Textile Auxiliaries, Dyes and Dye Intermediates Technology. Asia Pacific Business Press Inc. (2009)
26. Papazoglou, E.S.: Handbook of building materials for fire protection. In: Harper, C.A. (ed.) Chapter 4. McGraw-Hill, New York (2004)
27. Pinto, U., Yuan Visconte, L., Gallo, J., Reis Nunes, R.: Flame retardancy in thermoplastic polyurethane elastomers (TPU) with mica and aluminum trihydrate (ATH). Polym. Degrad. Stab. **69**(3), 1, 257–260 (2000)
28. Price, D., Liu, Y., Milnes, G. J., Hull, R., Kandola, B. K. and Horrocks, A. R.: An investigation into the mechanism of flame retardancy and smoke suppression by melamine in flexible polyurethane foam. Fire Mater., **26**, 201–206. (2002)
29. Quagliano, J.: Studies on incorporation of exfoliated bentonitic clays in polyurethane foams for increasing flame retardancy. International Conference on Structural Nano Composites (NANOSTRUC 2012) IOP Publishing IOP Conference Series: Materials Science and Engineering 40 (2012)
30. Sivriev, H., Borissov, G., Zabski, L., Walczyk, W., Jedlinski, Z.: Synthesis and studies of phosphorus-containing polyurethane foams based on tetrakis(hydroxymethyl) phosphonium chloride derivatives. J. Appl. Polym. Sci. **27**(11), 4137–4147 (1982)
31. Sivriev, H., Kaleva, V., Borissov, G., Zabski, L., Jedlinski, Z.: Rigid polyurethane foams with reduced flammability, modified with phosphorus- and nitrogen-containing polyol, obtained from tetrakis(hydroxymethyl)phosphonium chloride. Eur. Polym. J. **24**(4), 365–370 (1988)
32. Stefani, P., Esposito, L., Manfredi, L., Vazquez, A.: Mechanical properties of montmorillonite filled polyurethane foams. Conference on Science and Technology of Composite Materials COMAT, 169–170, Buenos Aires. ISBN: 987-544-162-7 (2005)

33. Thirumala, M., Khastgira, D., Singhaa, N., Manjunathb, B., Naik, Y.: Effect of a nanoclay on the mechanical, thermal and flame retardant properties of rigid polyurethane foam. J. Macromol. Sci., Part A 704–712 **46**(7) (2009)
34. Thirumala, M., Khastgira, D., Nando, G., Naik, Y., Singha, N.: Halogen-free flame retardant PUF: effect of melamine compounds on mechanical, thermal and flame retardant properties. Polym. Degrad. Stab. **95**, 1138–1145 (2010)
35. Valizadeh, M., Rezaei, M., Eyvazadeh, A.: Effect of nanoclay on the mechanical and thermal properties of rigid polyurethane/organoclay nanocomposite foams blown with cyclo and normal pentane mixture. Key Eng. Mater. **471–472**, 584 (2011)
36. Van der Veen, I., De Boaer, J.: Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. Chemosphere **88**, 1119–1153 (2012)
37. Wang, Z., Pinnavaia, T.: Nanolayer reinforcement of elastomeric polyurethane. Chem. Mater. **10**, 3969–3971 (1998)
38. Weil, E.: Flame retardants (Phosphorus Compounds). In: Grayson, M. (ed.) Kirk-Othmer Encyclopaedia of Chemical Technology, vol. 10, 3rd edn. Wiley Interscience, New York (1980)
39. Weil, E.: Phosphorus-containing polymers. In: Kroschwitz, J. (ed.) Encyclopaedia of Polymer Science and Engineering, vol. 11, pp. 96–126. Wiley, New York (1988)
40. Weil, E., Levchik, S.: Commercial flame retardancy of polyurethanes. J. Fire Sci. **22**, 183–209 (2004)
41. Weil, E., Levchik, S.: Flame Retardants for Plastics and Textiles: Practical Applications, p. 71. Carl Hansen, Munich (2009)
42. Yildiz, B., Seydibeyoglu, M., Guner, F.: Polyurethane–zinc borate composites with high oxidative stability and flame retardancy. Polym. Degrad. Stab. **94**(7), 1072–1075 (2009)
43. Zammarano, M.: Thermoset fire retardant nanocomposites. In: Morgan, A.B., Wilkie, C.A. (eds.) Flame Retardant Polymer Nanocomposites. Wiley, New York (2007)
44. Zhang, S., Horrocks, A.R.: A review of flame retardant polypropylene fibres. Prog. Polym. Sci. **11**(28), 1517–1538 (2003)
45. Zhu, W., Weil, E., Mukhopadhyay, S.: Intumescent Flame-Retardant System of Phosphates and 5,5,5′,5′,5″,5″-hexamethyltris(1,3,2,-dioxaphosphorinanemethan)amine 2,2′,2″-trioxide for Polyolefins. J. Appl. Polym. Sci. **62**, 2267–2280 (1996)