

Fireproof Nanocomposite Polyurethane Foams

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First introduced in 1954, polyurethane foams rapidly became popular because of light weight, high chemical stability, and outstanding sound and thermal insulation properties. Currently, polyurethane foam is widely applied in industrial and household products. Despite tremendous progress in the development of various formulations of versatile foams, their use is hindered due to high flammability. Fire retardant additives can be introduced into polyurethane foams to enhance their fireproof properties. Nanoscale materials employed as fire-retardant components of polyurethane foams have the potential to overcome this problem.

Keywords: polyurethane foams ; nanocomposite ; nanoparticles ; carbon nanomaterials

1. Carbon Nanomaterials as Fire Retardants

Carbon nanomaterials have been extensively applied as FRs in PUFs ^{[1][2][3][4][5][6]}. The flame retardant activity of carbon materials is caused by the following factors: CO₂ release during carbon oxidation, hindering of oxygen and combustible volatiles transmission between the polymer matrix and the external environment, significant heat isolation owing to formation of a char layer, as well as partial absorbance of smoke particles and combustible components ^{[7][8]}. FR carbon nanomaterials include carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphene and its oxide (GO), and expanded graphite (EG).

1.1. Carbon Nanotubes (CNTs)

CNTs are carbon allotropes which have a cylindrical shape and consist of one or several concentric graphite layers. The remarkable structural and electronic properties as well as the outstanding mechanical characteristics of CNTs (e.g., high aspect ratio, strength, and stiffness) have attracted particular attention in the development of PUF nanocomposites ^{[6][9][10][11]}.

However, recent reviews of the literature have revealed that the application of CNTs as fireproof components or as a component of an FR system is rather rare compared to other carbon nanomaterials ^{[2][6]}. Since pure nanotubes cannot provide proper flame retardancy of the final nanocomposites, CNTs are usually applied as a component of CFRs. Taking into account the negative charge of CNT surface and a great number of CNT surface modification approaches, the LbL technique seems to be the best option for PUF modification ^{[12][13][14][15]}. It should be noted that the LbL technique can create multilayer coatings on a charged substrate which is alternatively immersed into positively and negatively charged species. The electrostatic interaction between oppositely charged layers is the main driving force of this procedure; however, other interactions (e.g., donor/acceptor ^{[16][17]}, hydrogen bonding ^{[18][19]}, or covalent bonding ^{[20][21]}) can also be employed. Thus, the LbL technique is applicable for assembling a variety of materials such as polyelectrolytes, nanoparticles, or biomolecules ^[7].

Thus, for instance, aqueous CNT suspensions stabilized by using polyacrylic acid (PAA) and montmorillonite (MMT) were utilized as a component of bilayer (BL) coatings of flexible PUFs in ^{[13][14]}. In some cases, CNTs are modified/grafted for better interaction with other layers ^{[12][15]}. For example, CNTs modified by using branched polyethylenimine (PEI) had a better interaction with the PAA layer ^[15], whereas chitosan (CS) grafted CNTs, MMT, and alginate formed a trilayer (TL) structure ^[12].

The fire tests performed in the abovementioned studies revealed significant amelioration of the fireproof properties of the final composite foams. Fire tests demonstrated a tremendous reduction in the pHRR value of the final composite foam in ^[15]. Reductions in the pHRR and TSR values of 67% and 80%, respectively, were observed in the case of composite 6BL PUF and immediate self-extinguishing after flame removal in the case of 9BL PUF ^[13], whereas deposition of 20BL of polyaniline and MMT-stabilized CNTs led reductions in the pHRR, THR and TSR values of 51%, 37% and 47%, respectively ^[14]. The 4TL and 8TL PUFs revealed a dramatic reduction in the pHRR value (up to 69%) ^[12].

However, the application of CNTs is not limited to only the LbL technique. To provide better heat transfer of organic phase-change material (capric acid) encapsulated in PMMA capsules, the latter has been modified with CNTs and Fe_3O_4 nanoparticles [22]. In addition to heat transfer function, the CNT/ Fe_3O_4 component provided enhanced fire resistance of rigid PUF after its modification with obtained thermoregulating nanocomposite.

CNTs are not the only type of 1D carbon nanomaterials that can be employed as FRs in PUFs. For example, carbon nanofibers (CNFs) have been employed as AFR [23] and CFR [24] additives. Incorporation of CNFs into the polymer matrix led to a 35% reduction in the pHRR value compared to a control sample [23], while 4 BL coating consisting of CNF/PEI and PAA layers provided significant reductions in the pHRR and THR values (40% and 21%, respectively) and prominent burning time reduction (21%) [24]. Interestingly, the smaller CNF mass fraction in CFR (1.6% [24]) provided better fire protection than the larger CNF mass fraction (4%) embedded in the polymer matrix in a study by M. Zammarano et al. [23].

1.2. Graphene and Graphene Oxide

Graphene is another carbon allotrope which consists of a single layer of atoms arranged in a hexagonal lattice nanostructure [25]. Similar to CNTs, pristine graphene cannot provide the appropriate flame retardancy level for PUFs [26], hence, the common strategy is to apply it as a synergetic component in CFRs to enhance the effect of conventional FRs [6][7]. For instance, graphene nanoplatelets were applied in combination with nickel (II) oxide as AFR to improve fire retardancy of rigid PUF [26]. The fireproof components were added via an in situ polymerization method which led to an increase in foam density and enhancement of the mechanical properties (Young's modulus, tensile strength, and elongation at break). According to the fire tests, graphene provided a barrier effect, helping to prevent material consumption and flame diffusion, whereas NiO catalyzed CO oxidation to inflammable CO_2 . This synergetic effect resulted in an LOI increase to 30.5% and self-extinguished a sample containing only 2 wt.% of NiO and 1.5 wt.% of graphene.

Graphene oxide (GO) has wider applications as an FR than graphene since it has many oxygen-containing functional groups (e.g., OH, COOH, and epoxy group). GO particles in aqueous suspensions exhibit a negative charge, making GO an attractive nanomaterial for the LbL technique [27]. As a result, recently, GO has become a component of various multilayer CFRs [28][29][30][31][32][33][34][35][36][37][38][39]. The LbL technique requires PUF surface activation (positive or negative charging), which is usually achieved by treatment with diluted inorganic acids (e.g., HNO_3 [40]) or/and PAA [33]. Surface activation is followed by consecutive PUF dipping/immersion to either positively charged polymer solution (e.g., chitosan, dopamine) or negatively charged particle suspension (GO aqueous dispersion). Depending on the number of compounds employed, bilayer (BL), trilayer (TL), or even quadlayer (QL) coatings can be obtained. GO can be used along with other nanosized objects, for example, with $\beta\text{-FeOOH}$ nanorods [29] and amino-terminated silica nanospheres (KH-550-SiO_2) [41].

The stability of GO dispersion has considerable importance for GO-based CFRs. A possible GO coagulation may result in non-uniform distribution of FR in/onto PUF; hence, aqueous GO solutions are often stabilized, for instance, by sodium alginate (SA) [41].

Importantly, the LbL technique is not the only way to deposit GO-containing CFR. As an alternative, the electrostatic interaction of negatively charged GO with positively charged strong polyelectrolyte poly(diallyldimethylammonium chloride) (PDAC) was employed by Carosio et al. to coat the complete surface of a polymer matrix by using PDAC/GO exoskeleton comprising highly oriented GO nanoplatelets [32]. The 3BL coating suppressed flame spread and completely prevented foam ignition, whereas the 6BL coating withstood the penetration of a flame torch. In another study, FR nanocoating was obtained by oxidative polymerization of dopamine monomer within an aqueous liquid crystalline GO scaffold [31]. The PDA/GO nanocoatings were applied to PUF and significantly improved its fire resistance: a 65% reduction in the pHRR value at 5 wt.% PDA/GO loading in an 80 nm thick coating.

GO reduction (e.g., reduction of carboxyl groups) can significantly influence the interaction of the latter with other components of CFR [28][39]. Reduced GO (rGO) has better thermal stability than GO, and was employed in [28] to obtain fireproof PUF. The combination of both carbon nanomaterials can achieve high thermal stability owing to rGO and excellent fireproof properties owing to GO.

Functionalized GO (fGO) is usually grafted by using FR compounds, which provide certain additional fire retardant properties to the final product. For instance, nanocomposite PUF containing GO functionalized with 3-aminopropyltriethoxysilane and boric acid revealed stronger fireproof properties (pHRR of 182.2 kW/m^2) than that produced using non-functionalized GO (pHRR of 186 kW/m^2) [42]. In another work, the addition of fGO, obtained similarly to [42], to PUF led to an increase in the LOI value (from 27.5% to 28.1%) compared to PUF with GO [43]. Very recently, ionic liquid ([BMIM]PF₆) functionalized graphene oxide (ILGO) was synthesized and added to flexible PUF along with

other FRs [44]. The LOI and pHRR values of PUFs with ILGO and GO were 29.0% and 28.2%, and 98.56 and 130.77 kW/m², respectively. In these studies, the fGO showed better thermal stability and better flame retardance due to the presence of either boron or phosphorous compounds and catalyzation of char yield resulting in better barrier effect.

The fire alarm function is another fascinating property of GO-containing FRs, which, recently, has been extensively studied [45][46][47][48][49][50][51]. For example, flexible PUF was dip-coated using APP-modified GO [46]. The deposited CFR was reinforced using fluorine-containing silane for better fire retardancy. During burning, APP and silane decomposed, releasing elemental P, Si, and F, and thus, quenching radicals' diffusion, meanwhile GO acted as physical barrier and provided temperature-responsive resistance. The flame detection response time was only 2 s, whereas the fire early warning time in pre-combustion was 11.2 s at 300 °C. A multifunctional fire-resistant and fire-sensitive nanocomposite PUF/PVH/PA@GO/CNTs@PVH/PA/BN was obtained recently via the LbL technique [51]. The primer layer containing flame retardant copolymer (PVH) modified by phytic acid (PA) improved the PUF's surface flatness and flame retardancy. The middle layer composed of GO/CNTs served as a fire sensor to detect the temperature change. The surface layer of PVH/PA/boron nitride (BN) coating worked as a shield to protect the underlying sensor and promoted its temperature-response performance. Such a multilayer CFR provided outstanding fireproof properties of the final PUF nanocomposite: the LOI increased from 18 to 58% and the pHRR and THR values were reduced by 49% and 33%, respectively.

Summing up, the fireproof properties of graphene and its oxide are very close to those of CNTs. These carbon nanomaterials possess good thermal stability and outstanding mechanical properties and they are prone to form char layer which acts as a physical barrier to gas and heat diffusion via its high specific surface area. In combination with other FRs, graphene and GO improve the flame retardant property and smoke suppression effect of foam.

1.3. Expanded Graphite

Expandable graphite (EG) is one of the most efficient FRs for PUFs. It is synthesized during graphite intercalation with various acids (sulfuric, acetic, or nitric acids) [52]. The exposition of EG to high temperatures (>170 °C) results in tremendous volume expansion (~50–250 times [4]) because of simultaneous carbon oxidation and acid thermal decomposition followed by release of various gases (e.g., CO₂, SO₂, NO₂, etc.). Thus, EG can be considered to be a low cost one-component intumescent, implying that it combines an acid source, carbon source, and blowing agent [53].

As well as other carbon-based nanomaterials, EG is usually applied as and AFR in combination with other FRs, which leads to remarkable improvement of the overall fire retardant properties of nanocomposite PUFs [54][55][56][57][58][59][60][61][62][63][64][65][66][67][68][69][70][71][72][73][74][75][76][77][78][79][80][81][82][83][84][85][86]. Recently, the influence of EG particle size on fireproof properties has been investigated [61][62]. The 10 wt.% loading of EG particles with an average size of 300 µm and 500 µm led to an increase in the LOI of 29.8% and 31.8%, respectively, indicating that bigger EG flakes provide better fire retardancy. One of the possible explanations of these phenomena is that EG forms an interconnected structure in a foam matrix. Nevertheless, a usual high EG loading level [4] deteriorates some mechanical (e.g., decreased compressive strength) and isolating (e.g., higher foam density and increased open cell number lead to worse thermal conductivity) properties [2]. In particular cases, EG has been added as CFR [87][88]. Thus, S. Wang et al. [87] used a mixture of silicone resin (poly-DDPM) and EG to brush rigid PUFs. In addition to a significant increase in the LOI value (from 18% to 32.3%) and decreases in the PHR (by 55%) and the peak smoke release rate (by 59%), the compressive strength of the coated PUF was impressively increased (by 10%).

EG interfacial compatibility with the polymer matrix can be improved by using EG chemical modification/grafting (e.g., via epoxide and carboxylate groups [2][4]). As a result, EG links via hydrogen bonding with amino groups of such compounds as chitosan. Recently, this bonding was employed to coat flexible PUF using the dip-coating method [88]. In another work, EG was successfully bonded with SA to be used as an effective CFR [89]. Encapsulation of EG is an alternative strategy for interfacial compatibility improvement. For instance, EG encapsulation in magnesium hydroxide (MH) led to better interface adherence and considerably enhanced flame retardance of nanocomposite foam (LOI of 32.6%) [90]. Nevertheless, although interest in nanocomposite PUFs based on modified EG has been continuously growing, the number of studies on EG chemical modification is still rather limited [89][90][91][92][93][94][95][96].

2. Nanoclay Fire Retardants

2.1. One-Dimensional Nanoclays

Halloysite (or halloysite nanotubes (HNTs)) is a tubular (1D) aluminosilicate with the chemical formula Al₂(OH)₄Si₂O₅·4H₂O. Aluminosilicate nanosheets are rolled in such a way that the HNT exterior surface has a conner-shared tetrahedral SiO₄ layer, and thus, has a negative charge, whereas the nanotube lumen surface consists of an edge-

shared octahedral AlO_6 layer and is positively charged [97]. Sepiolite nanofibers have a layer of magnesium ions with octahedral coordination and two layers of silica in a tetrahedron; the chemical formula of sepiolite is $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH},\text{F})_2\cdot 6\text{H}_2\text{O}$. As well as HNTs, sepiolite fibers are negatively charged [98]. The outer surface of both NCs has the silanol groups (Si-OH) and can be chemically modified/grafted which can result in a change in the surface charge. Due to outstanding mechanical properties, high aspect ratio, surface area, and thermal stability, as well as negatively charged surface, and the possibility of its modification, one-dimensional NCs are considered to be affordable replacements for more expensive CNTs in various PU nanocomposites [99][100].

For instance, an SA-stabilized sepiolite aqueous solution and PEI were deposited on flexible PUF using the LbL technique [101]. The deposition of 6 BL (SA-sepiolite/PEI) led to a reduction in the pHRR and THR values from 710 to 170 kW/m^2 and from 32.6 to 24.8 MJ/m^2 , respectively. Smoke production was also considerably reduced (e.g., total smoke production reduction by 25%) owing to the formation of a uniform thick thermally resistant char/sepiolite layer impeding gas diffusion. During the last 5 years, HNTs have frequently been applied for improvement of PUF fire resistance [102][103][104][105][106]. F. Wu et al. [105] treated flexible PUF with an aqueous solution of HNTs using the dip-coating technique. The introduction of HNTs transferred the foam surfaces from hydrophobic to super-hydrophilic (contact angle decreases from 116° to 0° after HNT coating), improving thermal stability and fire resistance. The same flame retardant effect was observed in composite PUF after its coating with PEI/APP/HNT film [106]. The foam primarily activated with PAA was immersed in 4 wt.% PEI—8 wt.% APP—10 wt.% HNT solution for 1 min. Such an express coating procedure was enough to provide a reduction in the pHRR and THR values of 52.5% and 3%, respectively. It is noteworthy that the pristine foam and foam treated only with the PEI-APP solution displayed almost the same fireproof properties, indicating the key role of HNTs in the flame retardancy enhancement of the final composite. The presence of HNTs slows down fire spread via formation of a more stable char protection which preserves foam from further degradation.

Despite rather promising results demonstrated by nanocomposite PUFs treated with HNTs, in fire tests, flame retardancy can be increased with the help of chemical modification of the halloysite surface. For example, the HNT surface can be grafted by HDTMS and TEOS, giving polysiloxane-modified HNTs (POS@HNT) [104] or modified with branched PEI (BPEI), as has been accomplished by R.J. Smith et al. [103]. In addition to outstanding torch flame resistance during 10 s, the PUF coated by using POS@HNTs exhibited super-hydrophobicity, and therefore, it was possible to use nanocomposite PUFs for efficient and recyclable oil absorption [104]. At the same time, the LbL deposition of PAA-stabilized HNTs and BPEI-HNTs on the PUF surface resulted in a tremendous enhancement of fire retardance: CFR consisting of 5 BL reduced the pHRR value by 62% and the TSR value by 60%. HNTs act as barriers for mass and heat transfer, hence, significantly delaying flame spread and preventing melt dripping, without collapsing the foam structure [103].

The application of one-dimensional NCs as fire retardant components of composite PUFs is very similar to that of CNTs. NCs are rarely employed as a single FR component, being a synergist component of multicomponent FR. The negative surface charge and possibility of surface modification prompts the use of NCs as a component in CFR systems (e.g., LbL deposition). As a component of a CFR system, one-dimensional NCs can be referred to as non-intumescent agents that provide a shielding effect during polymer thermal decomposition, which slows down the transfer of heat, oxygen, mass, and volatile products. Remarkable suppression of smoke production can also be linked to formation of a uniform and stable barrier that impedes further gas diffusion as well as water release from NC structure at elevated temperatures.

2.2. Two-Dimensional Nanoclays

The group of two-dimensional NCs includes a number of materials: montmorillonite (MMT), kaolinite, vermiculite (VMT), bentonite, dellite, laponite, mica, and hydrotalcite (HT). Among these clays, MMT has attracted the interest of researchers as a promising natural FR additive. MMT is 2:1 clay, implying that two sheets composed of SiO_4 tetrahedra lay on either side of the sheet containing $\text{AlO}_6/\text{MgO}_6$ octahedra [107]. VMT has the same structure as MMT; however, it is a hydrated silicate mineral that expands on heating. Kaolinite has the same chemical formula as halloysite, nonetheless, unlike the latter, it is presented by 2D hexagonal crystals consisting of stacked layers [108]. The neighboring aluminosilicate layers in NCs are linked via van der Waals forces. The interlayer distances in NCs considerably vary from one material to another. For example, the widths of MMT and kaolinite interlayer spaces are 1.23 nm and 0.71 nm, respectively. The interlayer space of NCs can be intercalated by small molecules. Thus, the ultrasonic treatment of NC fillers in PU components (e.g., polyol) may lead to clay intercalation or even exfoliation, which finally results in better clay dispersion, and hence, more effective heat barrier effect [109]. Unlike the previously described NCs, HT refers to a layered double hydroxide (LDH) group. The bivalent and trivalent cations (usually presented by Mg^{2+} and Al^{3+}) are octahedrally coordinated to six hydroxyl groups and form a positively charged layer. The HT interlayer space contains water molecules and anions (usually

presented by CO_3^{2-}) which compensate for the positive charge. As well as other NCs, the interlayer space of HT can be modified by various inorganic and organic anions [110].

Layered NCs can be used as individual FRs. For instance, A. Agrawal et al. added kaolinite to polyol as AFR [111]. An aqueous solution of NC was treated using 1% APTES solution in order to improve the adhesion between the matrix and filler. The results of TGA and fire tests indicated enhancement of thermal stability and fireproof properties (reductions in pHRR, THR and TSR of 25%, 29% and 65% respectively) of nanocomposite foams. However, as well as other nano-sized components of composite PUFs reviewed above, layered NCs are usually applied in combination with other FRs. Thus, VMT/CS 8BL structure significantly reduced the pHRR and TSR values of flexible PUF by 53% and 63%, respectively [112]. High-aspect-ratio mica stabilized by PAA and CS have been used as components of BL coating for PUF [113]. The composite foam with 8 BL withstood a 10 s torch flame test and self-extinguished. The pHRR and TSR values were reduced by 54 and 76%, respectively, owing to reinforcement of the protective char layer by the mica particles. Such a reinforced char layer provides a better barrier effect, suppressing smoke release and impeding flammable gases and heat diffusion.

In another study, cationic starch and MMT were used as components of CFR introduced by using spray coating [114]. Despite the fact that the 5 BL structure did not inhibit flame propagation, it successfully prevented the melt from dripping and preserved the inner part of the foam. The pHRR and THR values were reduced by 22.7% and 52.7%, respectively. MMT can also become a component of more complex CFR systems. Thus, in [115], the PUF surface was firstly modified using alginate-stabilized MMT/CS/poly-D-lysine TL, and then, coated with CS-PA intumescent layer. Various flame resistance tests revealed outstanding improvement of nanocomposite PUF due to the synergetic effect of TL structure providing higher thermal stability and a more uniform coating and intumescent agent ensuring production of char isolating barrier. In some FR systems, MMT is not the only nano-sized component and it is used in combination with CNTs [12][14], GO [48], sepiolite [116] and other materials [117]. For instance, the modification of salvia filler with MMT particles considerably improved interphase compatibility between filler and the polymer matrix. This fact led to better filler dispersibility which finally resulted in well-developed foam structure and improved mechanical, thermal, and flame-retardant performances. Earlier various multilayer structures (BL, TL, and QL) including BPEI, PAA, sodium montmorillonite (Na-MMT), and LDH were deposited on the flexible PUF using the LbL technique [118]. The nanocomposite foam with the PAA/LDH/BPEI/Na-MMT quadlayer revealed a decrease in the pHRR value of 31% and a decrease in the THR value of 21%. The LbL approach was also employed very recently by S. Abrishamkar et al. [119] to coat flexible PUF using LDH and modified GO layers. The obtained composites demonstrated good mechanical properties, increased char yield, and outstanding improvement of the fire safety properties. Although the enhanced flame retardance was primarily caused by GO modification, it should be noted that LDH presence in the BL structure provided better interaction with modified GO, resulting in thicker and denser coating on the foam surface. In the work of H.-K. Peng et al. [120], non-modified HT mixed with phosphorous-based FR (FR-047) was used as AFR filler in rigid PUFs. Foam modification provided an increase in the LOI value of 4%. Again, the layered NC-reinforced char layer providing better barrier functions.

As mentioned above, the chemical modification of the interlayer space in layered NCs provides further improvement of fire retardant properties of clay-based FRs [121][122][123][124]. The chemical functionalization implies intercalation or even exfoliation of the layered NC. In the work of X. Zheng et al. [121], organically-modified montmorillonite (OMMT) mixed with phosphorous-containing APP and TPP was introduced as AFR in flexible PUF. Recently, OMMT was further functionalized with phosphorus-containing organosilicon compound (PCOC) which led to a significant increase in interlayer space and NC exfoliation [122]. According to the CCT results, additional functionalization of OMMT decreased the pHRR and TSR values by 51% and 40%, respectively, compared to neat foam and by 47% and 37%, respectively, compared to PUF/APP/OMMT. Such a significant difference between the CCT results for functionalized and non-functionalized OMMT is believed to be due to the higher degree of clay intercalation/exfoliation, hence, better clay distribution in the PU matrix, and thus, promotion of a denser and more uniform char layer. Phosphorous-containing agent was also introduced in HT interlayer space and the obtained composite was applied as AFR to flexible PUFs [124]. The provided CCT and LOI test revealed dramatic improvement in the fire resistance of composite foams, which can be explained through the synergetic effect of LDH and phosphoric acid, i.e., the crystal water contains LDH and absorbs the heat, and hence, lowers the temperature, meanwhile phosphoric acid promotes the carbonization reaction and oxygen isolation. The interlayer space of LDH has also been modified with sulfonate-containing calix[4]arenes [123]. Again, the obtained intercalated clay was employed as AFR filler for castor oil-based flexible PUFs. The authors noted that application of calix[4]arenes macrocycles improved LDH dispersion quality in the polymer matrix (as well as in [122]), which led to a higher char yield, and finally resulted in good smoke suppression and flame retardancy.

Taking into account the recent studies on the use of layered 2D NCs as FR additives in PUFs, one can note their multifunctionality. In addition to enhancement of the mechanical and thermal stability of the final composite, and hence, retardation of PUF thermal decomposition and release of flammable gases, the layered NCs can be intercalated/modified by various organic and inorganic substances which can act as additional FR agents. Thus, unlike one-dimensional NCs, two-dimensional NCs can be considered to be both intumescent and non-intumescent FR additives. The two-dimensional NCs used individually or as a component of multicomponent CFR systems revealed remarkable fireproof activity owing to the incorporation in the char barrier layer, thus, enhancing suppression of the gas/heat diffusion and retarding flame propagation.

3. Other Nanosized Fire Retardants

Obviously, the carbon nanomaterials and nanoclays mentioned above are not the only nanosized FR additives applied in composite fireproof PUFs. For instance, thermal stability and flame retardance of PUF have been improved after incorporation of basalt wastes ^[125]. Very recently, fly ash was employed to enhance fire resistance of PUFs ^{[126][127]}. It is noted that the incorporation of basalt wastes and fly ash in the PU matrix led to better thermal stability of the composite foam (hence, higher temperatures of PU thermal decomposition) and higher char yield. Inorganic nanomaterials such as nanoparticles (NPs) are another class of FR additives occasionally used in composite PUFs ^{[64][128][129][130][131][132][133][134][135]}. For example, silica NPs have been introduced in PUFs via sol-gel deposition ^{[128][130]}. In both studies, the PUFs were immersed in water solutions containing TEOS, ammonia solution, and alcohol. At the end of the reaction, TEOS transformed to silica gel, whereas freeze-drying in ^[130] turned it onto aerogel. Upon combustion, silica nanoparticles prevented dripping of flaming residues (observed for non-treated foams) via increasing polymer viscosity and formed a compact and stable silica-rich hybrid char layer. The barrier effect of the latter led to a significant decrease in the pHRR value (55% ^[128] and 40% ^[130]) and the THR value (21% ^[128] and 29% ^[130]) and inhibited the release of smoke and combustible gases. Earlier, a remarkable reduction in the pHRR value of 80% was observed for flexible PUF treated with alumina aerogel ^[135]. As well as other nanomaterials, NPs can be carriers of various FR additives. Composite AFRs were prepared by DOPO immobilization on the surface of silica aerogel ^[131] and TiO₂ NPs ^[129]. In these works, a dramatic increase in the fire resistance of final composite foams was achieved owing to the synergetic effect of nanoscale carriers and phosphorous-containing FR. Metal oxide NPs were applied in composite PUFs very recently ^{[132][133][134]}. The MgO and ZnO NPs added in combination with ATH increased the LOI values of the corresponding PUFs by 3% ^[133], whereas modification by CuO-loaded Fe₃O₄@ZIF-8 nanocomposite (where ZIF-8 is zeolitic imidazolate framework) decreased both magnetic properties and the pHRR value by 69% ^[134]. In addition to NPs, various two-dimensional inorganic nanomaterials have been tested as promising FRs. For instance, MXene (layered Ti₃C₂)/CS BLs were deposited on flexible PUF via the LbL technique ^[136]. According to an analysis of the burned samples, MXene nanosheets formed thermally stable flakes under elevated temperatures. Moreover, the formation of TiO₂ was observed, implying a decrease in the oxygen concentration in this zone. Newly formed TiO₂ could also serve as a catalyst of cross-linking and charring of CS and PU, thus, additionally improving fire safety performance.

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