For more than 60 years, polystyrene panels have been viewed as energy-saving insulating materials for new and refurbished buildings. For example the XPS panels with the brand names Styrofoam and Xenergy are used on inverted roofs. Here, the waterproofing layer is installed directly on the supporting structure, with the insulating layer on top of it (© Dow)

Flame Retardant with Molecular Anchor

Sustainable Alternative for Forbidden HBCD in Polystyrene Insulating Materials

Since August 2015, the flame retardant hexabromocyclododecane (HBCD) may not be used for insulating materials. After many years of research and development, an adequate substitute has been developed, which is suitable for extruded as well as expanded polystyrene foams. It is neither toxic nor bioaccumulative according to the European REACH regulation and the Stockholm Convention's worldwide POP (persistent organic pollutant) list.

Polystyrene foams (PS) are used worldwide as insulating materials in the construction industry, where they must comply with stringent regulations such as fire protection standards. With their products, the entire polystyrene foam industry prevents about 1.7 Gt of CO_2 greenhouse gas emissions [1, 2]. In Germany, more than 60 % of energy consumption occurs in buildings. Consequently, the savings potentials are accordingly high. To reduce energy consumption, the German Energy Saving Ordinance (EnEV) therefore specifies efficient thermal insulation for new buildings. Also in existing buildings, composite thermal insulation systems can cut heating costs, thereby also significantly reducing the emission of environmentally harmful gases.

Polystyrene foam, both extruded (XPS) as well as expanded (EPS), is a widely-used material with special properties such as low water absorption and high dimensional stability, that cannot be »

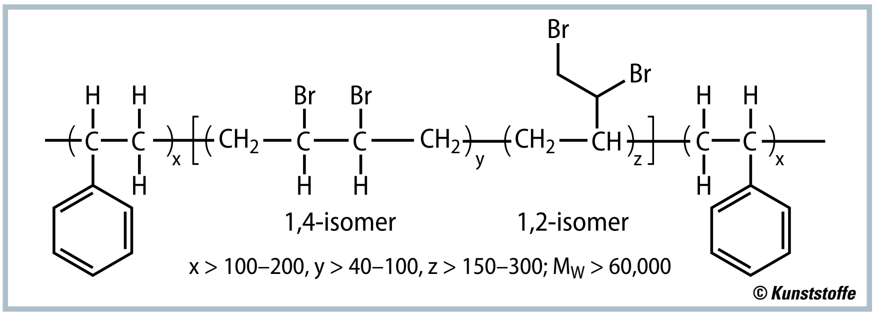

Fig. 1. The chemical structure of the polymeric flame retardant is a brominated styrene-butadiene-styrene block copolymer with a molecular weight of more than 60,000 g/mol and a 1.2 isomer fraction of >50 %. The higher molecular weight reduces the risk of migration through cell membranes (source: Dow)

replaced with other insulating materials. For many decades, small amounts of hexabromocyclododecane (HBCD) were added to PS foams as a fire retardant and flame resisting agent. However, since August 21, 2015, the European REACH regulation for chemicals forbids the use of HBCD in the European Union because it has been classified as a substance of very high concern (SVHC). Since then, HBCD may not be used in XPS, and the EPS industry was granted a two-year transitional period. Following the inclusion of the HBCD flame retardant in the POP list by the Stockholm Convention at the end of May 2013, the worldwide ban on HBCD in PS foams has become a hotly debated issue. So that PS foam could continue to be used as an efficient insulating material, a new flame retardant was necessary. On the one hand, the retardant must be ecologically compatible, and on the other, it must not have a negative effect on the established good properties of PS foam. For this purpose, Dow Chemical Company in Midland, Michigan/USA has developed the Bluedge Polymeric Flame Retardant Technology.

Balancing Act between Regulations, Environment, and Fire Protection

Since the start of the new millennium, the PS foam industry has been searching for a sustainable alternative for the flame retardant HBCD, which has been in use for decades. The new material was to have a significantly better health and non-toxic environmental profile, combined with efficient cost and similar properties as HBCD. In 2011, after many years of research and development work with more than a hundred trials, a highly diversified team of chemical experts, material scientists, engineers, and toxicologists succeeded in meeting these demands [3, 4, 5]. The result is a polymeric flame retardant, whose chemical structure is shown in **Figure 1**. Thanks to its controlled stability, it withstands the foaming process, but in case of a fire its chemical and structural design releases active flame retarding components. The flame retardant developed by Dow has been confirmed in numerous tests by the PS foam industry as the new fire protection standard for XPS as well as EPS foam. It finds the balance between increasingly tougher construction regulations in the field of energy-efficient materials, environmental compatibility, and existing fire prevention regulations.

Due to their persistent, bioaccumulative, and toxic properties (PBT substance) many flame retardants have a limited application range. The newly developed polymeric flame retardant has a molecular weight of more than 60,000 g/mol, which makes it 100 times higher than low-molecular flame retardants such as e.g. HBCD (**Fig. 2**). Consequently, there is only a minimum risk of migration through cell membranes, which usually leads to a lower toxicity potential. By nature, this makes the polymeric flame retardant more sustainable than small molecules, i.e. it is not a PBT substance.

The microstructure of the polymeric flame retardant is structured in such a way that it can be mixed with the PS foam matrix. For this, a styrene-butadiene-styrene (SBS) block copolymer with PS end groups was used as raw material (**Fig. 1**). These PS end groups lend good mechanical and fire-resistant properties to the PS foam. Moreover, they are firmly embedded in the foam matrix and cannot migrate. The double bond of average polybutadiene segments reacts completely with bromine, thereby forming the actual flame-resistant property of the polymeric flame retardant.

In a fire with very high temperatures bromine is released, thereby creating the flame retardant effect and preventing – or at least retarding – decomposition of the PS foam in case of a fire. The use of bromine chemistry as an active flame-retardant species resulted after numerous fruitless tests with other non-halogenated mechanisms of action based e.g. on phosphorus, sulfur, or nitrogen compounds.

For the market introduction, the use of existing processes and plants was essential. The polymeric flame retardant is the first type that is stable enough to withstand the extrusion process during the production of XPS foam, only requires marginal modifications in suspension polymerization during the production of EPS foam, and features very good flame-resistant properties in the PS foam [6].

Licensed Production of the Flame Retardant

Three globally active flame retardant producers – Israeli Chemicals Ltd. in Tel Aviv, Israel, Albemarle Corp. in Charlotte, North Carolina/USA, and Great Lakes Solution in West Lafayette, Indiana/USA (recently acquired by Lanxess AG, Cologne, Germany)

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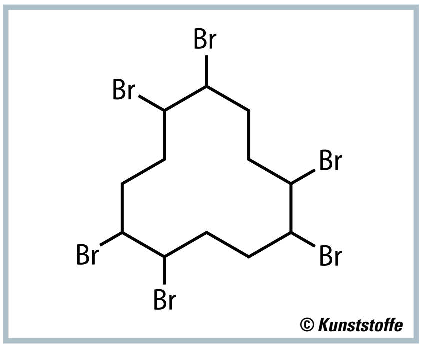

Fig. 2. Compared with the new development, the previously used and no longer permitted hexabromocyclododecane (HBCD) has a considerably lower molecular weight of 642 g/mol (source: Dow)

– produce the polymeric flame retardant under license, and market it worldwide [7–9]. Hereby, the producers are responsible for developing and providing the production capacities, and ensuring an adequate supply. In the production chain, the flame retardant producers come even before the raw material suppliers for the EPS foam industry, and also before the compounders, who supply the XPS foam industry.

The license holders and present producers and marketers of the polymeric flame retardants were and still are close partners during the product's commercialization. These include the German PS foam industry associations, the FPX trade association (Fachvereinigung Polystyrol-Extruderschaumstoff), and the German rigid foam industrial association (Industrieverband Hartschaum IVH), plus numerous end users including Dow with their XPS plants [10–13].

In Japan, the polymeric flame retardant is being used in XPS foam since 2014, following the ban of HBCD. Since the REACH regulation on HBCD in 2015, it is used in XPS foam in the European Union, and to a large extent it is used in EPS foam and in Canada since 2016. A predominant share of the PS foam industry has committed itself to replace HBCD with this more sustainable alternative in insulating materials. This conversion is carried out under control, so that the requirements for quality and product availability are met, and a smooth transition to the new flame retardant is ensured for the end users.

Comprehensive Environmental Testing

The polymeric flame retardant developed by Dow (**Figs. 1 and 3**) was subjected to an intensive health, environment, and toxicity-related testing program. The tests went beyond what is legally specified for polymers, to ensure that the sustainability aims are reached. Laboratory investigations supported by model calculations proved that the polymeric flame retardant is not a PBT substance.

The toxicologic examinations revealed only a minimum risk, and no indications of toxic, mutagenic, or carcinogenic properties (**Table 1**). This low toxicity is due to the high molecular weight and the associated low bioavailability, i.e. it cannot accumulate in organisms [14]. The molecule has been registered successfully in Europe (EU), Japan, USA, Canada, Korea, China, and Taiwan.

It must be pointed out here, that although the polymeric flame retardant has been classified as non-toxic and non-bioaccumulative, it is also highly stable and thereby persistent. The latter property has been selected intentionally, as it is essential in a long-term application such as building insulation to ensure that the flame retardant effect in the PS foam is still present after more than 50 years in the building.

Occasionally, the use of a brominated substance is considered to be undesirable. We wish to point out that even after intensive searching, no unhalogenated material could be found that offers an improved environmental and toxicologic profile for the PS foaming process and the product requirements.

In its 2014 "Design for the Environment Report" on FR alternatives for HBCD, the Environmental Protection Agency (EPA) confirmed the sustainable profile of the new polymeric flame retardant [15]. A survey of the health and environment-related properties is given in **Table 1**. The flame retardant developed by Dow is significantly different from other HBCD alternatives, which are based on low-molecular bromine structures and are listed »

Chemical structure	CAS number	Human toxicologic effects										Aquatic toxicity		Ecological toxicity	
		Acute toxicity	Carcinogen	Mutagenic	Reproductively harmful	Developmentally harmful	Neurologic	Repeated doses	Skin sensitizing	Eye irritant	Skin irritant	Acute	Chronic	Persistent	Bioaccumulative
Hexabromocyclododecane (HBCD)	3194-55-6	**L**	*M*	**L**	**M**	**H**	*M*	**M**	**L**	**VL**	**VL**	**VH**	**VH**	**H**	**VH**
Butadiene styrene brominated copolymer	1195978-93-8	**L**	*L*	**L**	**L**	**L**	*L*	**L**	**L**	**L**	**L**	**L**	*L*	*VH*	*L*
TBBPA-bis brominated ether derivative	97416-84-7	*L*	*M*	*M*	*M*	*M*	*L*	*M*	*L*	*L*	*L*	*L*	*L*	*H*	*H*
TBBPA bis(2,3-dobromopropyl) ether	21850-44-2	**L**	*M*	**M**	*M*	*M*	*L*	*M*	**L**	**L**	**L**	**L**	*L*	**VH**	*H*

VL = very low risk; **L** = low risk; **M** = medium risk; **H** = high risk; **VH** = very high risk. Colored letters refer to empiric data. Black italic letters refer to modeled data or professional assessments.

Table 1. Excerpt from the EPA risk report [14] on HBCD substitute materials and their health and environment-related properties (source: Dow)

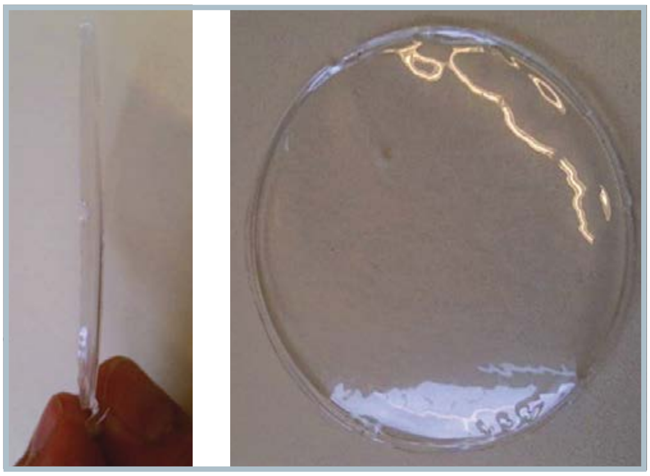

Fig. 3. The new sustainable flame retardant, shown here in pure form as a film, is itself a plastic or polymer with thermoplastic properties (© BASF)

for comparison. Also this report confirms that so far, no unbrominated alternatives have been identified in PS foam.

PS foam with the polymeric flame retardant is recyclable – e.g. for the production of EPS and XPS foam, in other applications, or it can be disposed of as non-toxic waste in conventional waste management procedures. All these properties underline the importance of sustainable PS insulating materials using Dow's polymeric flame retardants.

Conclusion

The new flame retardant is used in PS foams in amounts of only 1–3 wt.%. Comprehensive testing programs by the industry, together with the German industrial associations (Fachvereinigung Polystyrol-Extruderschaumstoff (FPX), the Industrieverband Hartschaum (IVH)), the European association of PS foam producers (Exiba) as well as the Institute for Thermal Insulation (FIW) in Munich with participation of the German Institute for Building Technology (DIBt) in Berlin showed: The substitution of HBCD with a polymeric flame retardant has no effects on the thermal insulating and physical properties of XPS and EPS insulating materials. The fire behavior of EPS and XPS insulating materials is completely maintained. Since August 2017, the entire European PS foam industry is HBCD-free. ■

High-Performance Compounds

Compounds for Large Format Additive Manufacturing

At formnext, International exhibition and conference on the next generation of manufacturing technologies, **Sabic** introduced to the European market a family of high-performance Thermocomp AM compounds to address the unique requirements of large format additive manufacturing. Because they are reinforced with carbon or glass fibers for added strength, the new compounds can be used for demanding applications in the tooling, aerospace, automotive and defense industries.

A new family of high-performance Thermocomp AM compounds addresses the unique requirements of large format additive manufacturing (LFAM) (© Sabic)

Sabic's first eight reinforced Thermocomp AM compounds for large format additive manufacturing are based on four of the company's amorphous resins: acrylonitrile-butadiene-styrene (ABS), polyphenylene ether (PPE), polycarbonate (PC) and polyetherimide (PEI). These resins exhibit good creep behavior versus semi-crystalline resins, and reduced deformation under constant pressure. Further, these materials exhibit lower shrinkage during cooling, which means greater dimensional stability and less thermal expansion during part use. Each of the Thermocomp AM materials is reinforced with carbon or glass fiber, depending on the degree of stiffness and dimensional stability required.

At formnext in Frankfurt/Main, Germany, Sabic was showcasing a section of a yacht hull from Livrea Yacht that was printed on the company's BAAM machine in its Center of Excellence for Additive Manufacturing in Pittsfield, MA/USA. The hull is a result of a collaborative design effort between Sabic, Livrea Yacht and 3D design and engineering software provider, Autodesk. Using Autodesk Fusion 360 design software and Sabic's processing expertise on the BAAM equipment, the three companies selected two materials from the Thermocomp AM portfolio: a carbon-fiber-reinforced PPE compound for the hull's outer layer, and a carbon-fiber-reinforced PEI for the inner lattice support structure.

Two materials from the new Thermocomp AM portfolio were selected for a yacht hull from Livrea Yachts – a carbon-fiber-reinforced PPE compound for the hull's outer layer, and carbon-fiber-reinforced PEI for the inner lattice support structure (© Sabic)

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