SABIC's Inputs to the Public Consultation Comments to Annex XV PFAS Restriction Proposal

Question number 6: Missing uses - PTFE used as an Anti-Drip Additive in Thin-Wall, Flame Retardant Polycarbonate Resins

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Executive Summary

Flame retardant polycarbonate resins used in thin-wall (thickness <1.0 mm) consumer electronics applications plays a critical role in consumer safety and requires the use of PTFE as an anti-drip additive. Thin walled parts reduce the amount of plastic used and therefore the amount of plastic waste produced during the manufacturing process as well as at the electronic devices' end of life. Before these tough thin-wall flame retardant polycarbonates were available, typical wall thicknesses in consumer electronics were 2-3 mm, which in comparison can lead to a 100% to 200% increase in resource consumption and solid waste generation, depending upon the electronic application design requirements. Thin-walled polycarbonate resins can also lead to lighter products which require less energy for transportation, which results in less CO_2 emissions.

Alongside many unique properties, polycarbonate is an inherently tough material which provides device integrity during and after an impact event, so that the electronic device can continue to function, and does not produce an electrical hazard (short circuit, shock hazard) or a fire hazard. There are no alternative engineering plastics available today that provide the necessary combination of impact resistance, ductility, and flammability properties for thin walled (<1 mm) electronic device parts.

To ensure that thin-walled polycarbonate resins have adequate flame retardancy, it is essential to use PTFE as the anti-drip agent. PTFE, in combination with flame retardant additives, increases the ignition resistance of the polycarbonate thereby lowering the probability of a fire event. If a flame event does occur, the unique properties of PTFE help prevent flames from spreading and allow individuals more time to escape a fire. Our extensive research has not found any alternatives that provide adequate flammability performance for thin-walled polycarbonate while also maintaining adequate impact resistance and ductility.

Given the absence of alternatives we feel it would be appropriate to allow for a 13.5-year derogation to have sufficient time to invent new materials or develop viable alternatives for PTFE used as an anti-drip additive in flame retardant polycarbonate resin formulations.

1. Substance Information

Substance Name: Poly(1,1,2,2-tetrafluoroethylene)
Synonyms/Abbreviations: PTFE
Molecular formula: $(C_2F_4)_n$
EC/List no.: 618-337-2
CAS number: 9002-84-0
Type: Solid

2. Introduction to thin-wall, flame retardant polycarbonate resins

This application relates specifically to injection mouldable polycarbonate resins, polycarbonate blends and polycarbonate copolymer resins (hereafter, "polycarbonate resins") designed for thin wall (wall thickness < 1.0 mm) flame resistant enclosures, structural components and/or insulators for the consumer electronics industry. Thin walled parts produced from these types of polycarbonate resins reduce the amount of plastic used and therefore the amount of plastic waste produced during the manufacturing process as well as at the electronic devices' end of life. Before these tough thin-wall flame retardant polycarbonates were available, typical wall thicknesses in consumer electronics were 2-3 mm, which in comparison can lead to a 100% to 200% increase in resource consumption and solid waste generation, depending upon the electronic application design requirements. Thin-walled polycarbonate can also lead to lighter products which require less energy for transportation, which results in less CO_2 emissions.

Flame retardant polycarbonate resin formulations are used in thin-wall applications where product safety (mitigated risk of flame/fire and/or electrical shock) is of utmost importance to the application. These resins and compounds are commonly used in devices where a potential fire/flame hazard exists, they play a critical role in consumer product safety as they help mitigate the risk of initial combustion and fire spread in these consumer and industrial devices/applications. Because of the extraordinary combination of mechanical, electrical, and flammability properties, flame retardant polycarbonates have become increasingly used in just about every electronic device. Electronic devices often rely on unique combinations of properties that polycarbonate resin formulations can have, including mechanical/impact strength, electrical insulation, flame resistance, corrosion resistance, integral (no-paint) color, and weather resistance. Depending upon the end use application, any combination of these properties could be the deciding factor for using polycarbonate resins versus other thermoplastic materials. For instance, consumer electronics often

need lightweight, molded-in functionality with impact, electrical, and flame resistance that alternate thermoplastic materials cannot meet.

3. Product safety standards

Nearly all electronic devices have an inherent risk of fire and a risk of shock. Product safety standards use material fire resistance and electrical insulation requirements as two critical safety elements to help mitigate these risks. For fire resistance, there are several common industry test standards that require materials to resist ignition, burning, and the dripping of flaming particles. One common standard is "*UL 94, the Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances*" which is now harmonized with the IEC 60707, 60695-11-10 and 60695-11-20 standards and the ISO 9772 and 9773 standards that are used to demonstrate compliance to flame retardant requirements in the EU. There are 6 flame classifications of materials that are used in enclosures, structural parts and electrical insulators in electrical devices: HB, V-2, V-1, V-0, 5VA and 5VB. The higher ratings – V-1, V-0, 5VA and 5VB - all require that samples do not drip flaming particles.

Since polycarbonate is designed to be shaped/flowed by heat, direct flame application can lead to melting and dripping of the polycarbonate before or during ignition. Any flaming melting/dripping has the chance of spreading flaming material beyond the initial ignition event and is almost always more pronounced in thinner rather than thicker walls. PTFE is the only viable additive for polycarbonate resins used in thin walls that can inhibit dripping **and** retain all the impact resistance and ductility properties which are essential for product safety and compliance with regulatory requirements.

During melting and shaping of the polycarbonate into injection molded parts, the PTFE does not melt and instead undergoes a physical form change from being semi-spherical particles to highly elongated fibrils. These long fibrils form an entangled network inside the polycarbonate resin matrix. During a flame event, this network of PTFE fibrils does not burn/ignite and instead helps promote char formation and provides much higher melt strength to the thin polycarbonate wall. PTFE as an anti-drip agent is typically used in the range of 0.1-0.5% by weight of the total polycarbonate resin formulation.

4. Why there are no alternatives to polycarbonate resins: Toughness

In addition to flame resistance, it is essential for product safety that thin plastic walls have adequate toughness to

- provide a durable product that does not break during normal use, including drops and other foreseeable events
- ensure safety by avoiding exposure of live circuitry, and
- meet EU regulatory requirements of the electrical device.

Toughness is comprised of a combination of two physical properties: impact resistance and ductility. Impact resistance is the material's ability to absorb shock or impact energy without breaking. Ductility is the material's ability to stretch without breaking.

A material's impact resistance and ductility can be measured using Notched Izod Impact (NII) and Tensile Elongation (TE). These techniques measure the amount of energy a material can absorb during impact and the percentage amount the material will stretch before breaking in controlled laboratory settings, following standardized test methods (e.g., ASTM D256[1]/ ISO 180[2] for NII and ASTM D639[3]/ISO 527[4] for TE). The higher the impact resistance and the ductility, the tougher the material is and the more resistant it is to cracking or breaking.

As highlighted in Table 1 polycarbonate resin formulations provide unmatched impact resistance and ductility in the afore-mentioned tests compared to other engineering plastics, while also providing the required flame resistance, as measured by the ability to pass UL94 V0 flame testing at less than 1.0 mm thickness. The other engineering plastics in the below table were selected, based on our technical expertise, as most likely to represent viable alternatives to polycarbonate resin formulations. However, as described below, none of these other thermoplastics represent viable alternatives to polycarbonates based on our research.

[1] Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics (astm.org)
[2] ISO 180:2019 - Plastics — Determination of Izod impact strength
[3] Standard Test Method for Tensile Properties of Plastics (astm.org)
[4] ISO 527-1:2019 - Plastics — Determination of tensile properties — Part 1: General principles

Material (non-reinforced)	Property Comparison			
	Property	**Flame Resistance**	**Impact/Crack Resistance**	**Ductility**
		Passes UL94 V-0 @<1.0 mm?	Notched Izod Impact, % of Reference	Elongation @Break, % of Reference
	Polycarbonate Blend	☑	100% (Ref)	100% (Ref)
	Nylon	☑	4% (96% decrease)	4% (96% decrease)
	PPE/PS	☑	12% (88% decrease)	14% (86% decrease)
	Polyetherimide	☑	4% (96% decrease)	55% (45% decrease)
	PPSU	☑	83% (17% decrease)	55% (45% decrease)
	PEEK	☒	11% (89% decrease)	46% (54% decrease)
	Polypropylene	☒	4% (96% decrease)	120% (20% increase)

Table 1. Flame resistance, impact resistance and ductility of engineering plastics compared to polycarbonate

As can be seen in Table 1, several materials can achieve similar flame resistance to the polycarbonate, however none of these materials have a comparable combination of both impact resistance and ductility (hence, overall toughness).

5. Why there are no alternatives to PTFE for thin wall polycarbonate

There are several strategies that can be employed to increase resistance to flame dripping by increasing the melt strength or the stiffness of the material with either viscosity enhancers or mechanical fillers. However, Table 2 highlights that none of these strategies can provide the necessary flammability performance for thin-walled polycarbonate while also maintaining adequate impact resistance and ductility.

Highly branched/high viscosity polycarbonate can increase the melt strength and reduce flame dripping. However, this results in a significant reduction in impact resistance and ductility by 86% and 56% respectively and does not provide adequate overall flammability performance at less than 1.0 mm wall thicknesses.

Glass fiber or other inorganic fillers (Clay, Talc, Carbon Fiber) can be added to increase the stiffness of the material and reduce flame dripping. However, these additives must be used at relatively high loadings (20-50% or more by weight) to have a significant effect on flame dripping properties, and these high loadings cause a dramatic decrease in the ductility and impact resistance of the material. Glass, Talc and Clay fillers, at 20 weight % loading significantly reduce the impact resistance and ductility by 84% and 96% respectively (and these properties will continue to deteriorate as filler loading increases), and do not provide adequate overall flammability performance at less than 1.0 mm wall thicknesses. Carbon fiber does provide adequate overall flammability performance at less than 1.0 mm wall thicknesses but significantly reduces the impact resistance and ductility by 90% and 99% respectively.

Property Comparison in PC

PTFE Replacement	Property	Flame Resistance	Impact/Crack Resistance	Ductility
		Passes UL94 V-0 @<1.0 mm?	Notched Izod Impact, % of Reference	Elongation @Break, % of Reference
	PTFE	☑	100% (Ref)	100% (Ref)
	Branched/High Viscosity Resin	☒	14% (86% decrease)	44% (56% decrease)
	Mineral (Glass, Talc, Clay)	☒	16% (84% decrease)	4% (96% decrease)
	Carbon Fiber	☑	10% (90% decrease)	1% (99% decrease)

Table 2. Flame resistance, impact resistance and ductility of alternative anti-drip agents compared to PTFE in polycarbonate

As can be seen in the table, only one alternative approach to PTFE (carbon fiber) can achieve adequate overall flammability performance, however the significant reduction in impact resistance and ductility does not allow it to meet product safety requirements and so this approach cannot be used in design and manufacture of consumer electronics.

6. Proposed text for derogation for thin-wall, flame retardant polycarbonate resins

There are no alternatives to PTFE available today for thin-wall flame retardant polycarbonate resins. A wide range of potential alternatives have already been tested and found to fail to provide the necessary properties. A new round of extensive, fundamental laboratory research will be needed to attempt to identify a completely new material, unknown today, that may potentially be developed into an alternative to PTFE. We expect it may take up to 8 years to carry out this basic research.

If a new alternative material is identified it would take several more years to test, qualify, certify, and start manufacturing parts from this replacement material. Companies may need to make changes to their manufacturing equipment and processes to use the new material in their injection moulding lines. These changes to manufacturing equipment and processes may be significant and require extensive time and capital investment.

Product requalification is a very time-consuming exercise which will require extensive resources over many years. The completion of this task will require sufficient test house capacity and transition time to requalify all existing thin-wall flame retardant polycarbonate resin parts in products which are used in Europe for safety and performance. For a company with a wide range of existing product designs, we estimate it could take up to 5 years to carry out the necessary manufacturing equipment changes and product re-qualifications.

In view of this, we recommend a minimum 13.5 year derogation for flame retardant polycarbonate resins for the production of thin walled parts, as follows:

[xx]. Paragraph 2(c) shall apply from (13.5 years after EIF) to flame retardant polycarbonate resins for the production of thin walled parts

7. Additional information on PFAS emissions from PTFE

No PTFE is released from parts manufactured from thin wall polycarbonates during their use phase. There is a considerable amount of data demonstrating

that PTFE itself does not release substances of toxicological or environmental concern during use[5].

At end-of-life, when these articles containing 0.1-0.5 weight% of PTFE in the polycarbonate matrix will eventually enter the waste stage, the amount of PFAS emissions depends on the waste (pre-) treatment method, e.g., recycling/re-use, landfilling and incineration. However, PTFE is a fluoropolymer that is not water soluble and therefore does not present the specific hazards which are found with non-polymeric PFAS.

PTFE is chemically, thermally, and biologically stable and therefore is not expected to transform to dispersive nonpolymeric PFAS when disposed of in a landfill. A recent study presented results[5] from OECD guideline biodegradation studies demonstrating that PTFE is stable and does not degrade to non-polymeric PFAS under environmentally relevant conditions. Further, PTFE meets the criteria to be considered a Polymer of Low Concern, PLC, which has negligible leachables, unreacted monomers, and oligomers most likely destroyed in use processing and would therefore not be expected to significantly contribute to landfill leachate.

Available data reveal[5] that PTFE is mineralized (i.e., all C–F bonds broken, hydrofluoric acid generated, and scrubbed to calcium fluoride) under commercial Waste-to-Energy (WtE) incineration operating conditions. In recent pilot scale studies[5] representative of full-scale WtE facilities, the most common form of end-of-life destruction conducted on PTFE found that combustion converted the fluorine into controllable hydrogen fluoride gas and that no fluorine-containing products of incomplete combustion were produced above background levels. Further, a recent study by RIVM[6] investigating the presence of PFAS in waste incinerator flue gas stated: “based on a literature review, RIVM expects that most of the PFASs will largely degrade during the incineration process and then be removed when the flue gases are cleaned. The remaining PFASs are expected to be removed during the recovery of the carbon dioxide”. The RIVM report affirmed that PTFE is the most stable fluorine-containing polymer. For PTFE, the RIVM report concluded that complete thermal decomposition is achieved at a temperature of approximately 800 °C.

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[5] Korzeniowski, S.H., Buck, R.C., Newkold, R.M., kassmi, A.E., Laganis, E., Matsuoka, Y., Dinelli, B., Beauchet, S., Adamsky, F., Weilandt, K., Soni, V.K., Kapoor, D., Gunasekar, P., Malvasi, M., Brinati, G. and Musio, S. (2023), A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers. Integr Environ Assess Manag, 19: 326-354. https://doi.org/10.1002/ieam.4646

[6] Bakker, J., Bokkers, B., & Broekman, M. (2021). Per- and polyfluorinated substances in waste incinerator flue gases (RIVM Report 2021-0143). https://www.rivm.nl/bibliotheek/rapporten/2021-0143.pdf