Technical article

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Flame-retardant TPEs with adhesion to polyamides

Custom-engineered thermoplastic elastomers with halogen-free flame-retardant technology make it possible to produce hard/soft components with direct adhesion to PA

By Martina Hetterich & Dirk Butschkau, KRAIBURG TPE

The increasing use of thermoplastic elastomers (TPEs) in multi-component applications with thermoplastics requires a solid understanding of the influences that affect the adhesion properties. This applies in particular if the hard component is a polyamide and the application requires a high level of fire protection. The following article explains the issue and the state of technology.

For decades, the polyamides market has seen continuous growth, with more and more compounds being modified and optimized according to customer-specific requirements. At the same time, there is a stronger trend toward the integration of functional properties in many application areas that only elastomers provide, such as vibration and sound damping, soft-touch effects, sealing against ambient influences and surfaces that provide good grip.

The immense variety of polyamide types and their various compositions are a special challenge in selecting material for appropriate hard/soft combinations. This applies even more to injection molding applications made of flame-retardant polyamide combined with a thermoplastic elastomer that is also flame-retardant.

Well-established halogen-free flame-retardant properties

KRAIBURG TPE has extensive experience in the development of TPEs with halogen-free flame-retardant properties.

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Technical article

A second product series with a V-0 nonflammability classification at wall thicknesses of 1.5mm in accordance with UL standard 94 V-0 has recently been introduced for multi-component applications with polypropylene. A further series with V-0 classification at 3mm has been a successful part of the product line for some time, and the next product series is now about to be launched. Due to high demand, KRAIBURG TPE is expanding its portfolio with a flame-retardant PA adhesion series. However, KRAIBURG TPE's specialists faced several challenges in developing these materials. The results of adhesion tests showed a significant spread, which is attributed to different settings and modifications of flame-retardant polyamide formulations.

More than a dozen different PA compounds with UL94 V-2 up to V-0 classification were tested in the course of the development work. As the project progressed, the tests focused on halogen-free flame-retardant materials that are V-0 classified, as these two properties are playing a more and more important role in decisive areas of application such as electrical engineering and electronics.

UL94 V-0 listed materials are self-extinguishing in case of fire and don't form into burning drops. The materials meet these requirements even without halogenated flame-retardants being used. KRAIBURG TPE materials comply with the IEC 61249-2-21 standard's definition of halogen-free.

If a fire breaks out, this means more safety for people involved, as less disorientating smoke develops and the flue gas is less toxic. In addition, flame retardants that are free of chlorine and bromine minimize the potential risk of damage to furniture and the building fabric caused by corrosive flue gases that develop when halogenated substances are burnt. In addition, their corrosiveness can even have a negative impact on maintaining the properties of old materials and their commercial usability, for example when recycling used cars.

Widely varying test results

The adhesive strength was tested on five specimens of each material combination using a tensile strength testing machine in order to determine the TPEs' peeling resistance in accordance with the VDI 2019 standard. For the test, the specimen is mounted on a movable carriage and the soft component is pulled vertically upwards via a deflection pulley at a speed of 100mm/min. A peeling resistance of at least 2.5N/mm was set as the target.

As was expected, adhesion testing of TPE/PA combinations provided widely varying results in this flame retardancy range, depending on the polyamide formulation (figure 1). Some polyamides show good adhesion, but in others it is insufficient. The essential factor here is the modification of polyamides with appropriate flame retardants and additives. Cross-checks with TPEs that don't contain flame retardants and basically show good adhesion to non-flame retardant polyamide types provide similar results. Research carried out by KRAIBURG TPE together with selected polyamide manufacturers confirms that the reason why such a TPE/PA combination fails to adhere is to be found in the polyamide.

Complex adhesion mechanism

It has already been found in previous adhesion experiments with non-flame retardant TPE/PA samples that good binding may apparently be impaired by glass fiber accumulations on the cut surface. Impact-resistant modifiers, stabilizers, colors, dispersants, separating agents and processing aids that migrate to the surface and thus impair the wetting and anchoring of the materials are regarded as other potential influencing variables.

Along with the formulation of the polyamide, the flame retardant's temperature sensitivity is a major challenge. In multi-component applications, non-flame retardant TPEs are frequently processed at temperatures of 240°C to achieve optimal adhesion.

Technical article

KRAIBURG TPE's newly developed flame-retardant materials have shown optimal adhesion at a relatively low melt temperature of 190°C, which accommodates the temperature sensitivity of the flame retardants.

As a general rule, the evaluation of adhesion quality has to take into account the break pattern along with the value actually measured for peeling resistance. Due to their reduced mechanical properties as compared to adhesion-optimized compounds without flame retardancy, the flame-retardant materials show lower adhesion values despite cohesive failure (break pattern D).

Custom-engineered solutions

The tests have nevertheless shown that, in specific cases, excellent adhesion to flame retardant PA can also be achieved with flame-retardant TPEs within a hardness range starting at 60 Shore A. The key to this lies in testing the materials combinations that are being considered as early as possible, in order to exclude incompatible compound partners even before the prototype phase and to identify more appropriate TPE/PA combinations in a targeted way. KRAIBURG TPE not only has the appropriate facilities and development competence for such projects, but can also on request provide a test report on the tested adhesion properties in accordance with relevant standards such as VDI 2019.

Appendix 2 summarizes the key properties of two THERMOLAST® compounds that have performed best in the adhesion tests. Both materials are classified as V-0 starting from wall thicknesses of 3mm and provide very good processing properties in injection molding. The color of these compound is natural, they can be individually colored.

The wide range of potential multi-component applications made of flame-retardant TPE/PA combinations in electrical engineering and electronics extends from plug-in connectors, to relay components and circuit breakers, as well as switch boxes and cable bushings. Further possible important areas of application are motor vehicles, commercial vehicles, rail vehicles and aircraft, as well as construction and building technology.

KRAIBURG TPE will once again be presenting itself as the competence leader in the thermoplastic elastomer (TPE) market during the forthcoming K 2019 from 16 to 23 October in Düsseldorf. At Stand C58-4 in the "Gummistraße" in Hall 6 and at the "Innovation Center" Stand E22, also in Hall 6, the manufacturer will address key challenges and trends in the growing TPE business.

Conclusion

The diverse range of modified polyamides and their different compositions make it harder to select suitable compounds for multi-component applications with TPEs, especially if the material properties required include high nonflammability. In order to find the best possible hart/soft combination with secure adhesion and halogen-free flame protection, thorough compatibility tests are required that are based on a solid understanding of adhesion mechanisms and on how additives affect adhesion. Ideally, processors and end-users should therefore have material suppliers involved at as early as possible a stage during the process of application development, in order to avoid expensive surprises and ensure that their products will be launched on schedule. KRAIBURG TPE has extensive expertise in formulating flame-retardant TPEs and making them reliably compatible for creating compounds with polyamides, and also supports its customers with relevant adhesion tests in accordance with the VDI 2019 standard. With this extension it is possible to extend application areas and market opportunities.

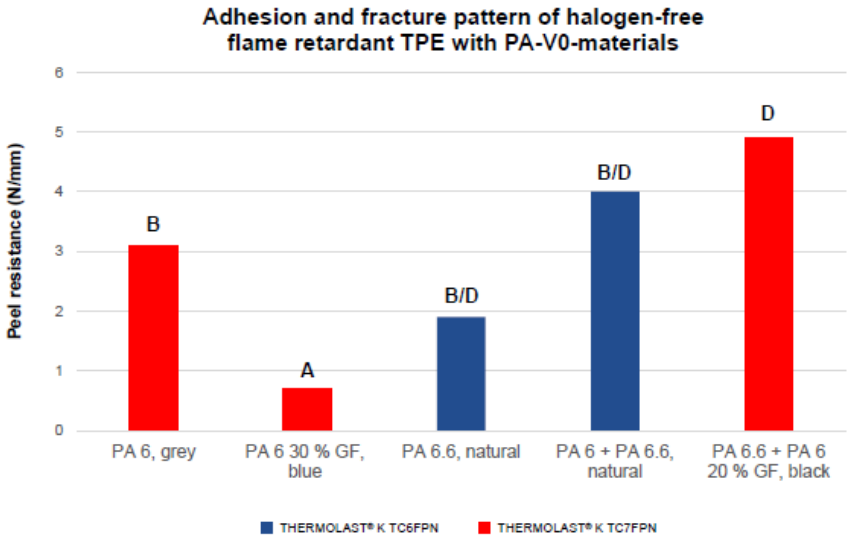
The authors

Martina Hetterich, who holds a degree in engineering (University of Applied Sciences), took over the position of Advance Development Engineer in 2015. Her main responsibilities include analyzing technical potentials of projects as well as managing and working on in-house material development projects. Martina Hetterich also coordinates the transfer of new products to the local development organizations and gives training courses on their findings. She started her career with KRAIBURG TPE in 2014. As a member of Team Development & Consumer, she worked on in-house and customer-specific materials development projects and provided technical support for the sales teams. She also created new formulations for thermoplastic elastomers with relevant conformities for the consumer and medical markets.

Dirk Butschkau, who holds a degree in engineering (University of Applied Sciences), is Head of Business Development EMEA with KRAIBURG TPE in Waldkraiburg and, in this position, is responsible for the introduction and commercialization of thermoplastic elastomers (TPEs) in Europe, the Middle East and Africa. His responsibilities include market-wide analyses of situation, demand and requirements for the implementation of new TPE concepts. Mr. Butschkau also works on developing and implementing strategic company projects. Mr. Butschkau started his career with KRAIBURG TPE in May 1999 as a sales and application engineer for sealing profiles and industrial applications. After holding several other positions such as head of Team Consumer and member of the company's project management department in Asia, he was Director of Business Development and responsible for sales in China and East Asia.

Technical article

Appendix 1



The adhesiveness of halogen-free flame-retardant types of TPE that are combined with flame-retardant polyamide depends to a large degree on the specific PA formulation. The development goal was to achieve a peeling resistance of 2.5N/mm, tested in accordance with VDI 2019.
(Image © KRAIBURG TPE)

Technical article

Appendix 2

Flame-retardant TPEs for multi-component applications with PA

Product Features		**THERMOLAST® K**	
		TC6FPN	**TC7FPN**
Color		Natural color / according to customer specification	
Properties	**Test method**		
Density	DIN EN ISO 1183-1	1.05g/cm³	1.05g/cm³
Hardness	DIN ISO 7619-1	62 Shore A	69 Shore A
Tensile strength[1]	DIN 53504/ISO 37	3.0MPa	3.0MPa
Elongation at break[1]	DIN 53504/ISO 37	291%	342%
Resistance to tear propagation	ISO 34-1 B (b) (Graves)	17.1N/mm	17.5N/mm
Adhesion to PA6[2]	**VDI 2019**	**~ 4N/mm (D)**	**~ 4.9N/mm (D)**
Nonflammability	**UL94**	**V-0 at wall thicknesses of 3mm**	

[1] Notwithstanding ISO 37, tested at a feed rate of 200 mm/min
[2] Depending on specific PA formulation, glass fiber content, modifiers and processing aids

Appendix 3. (Image: © 2019 KRAIBURG TPE)

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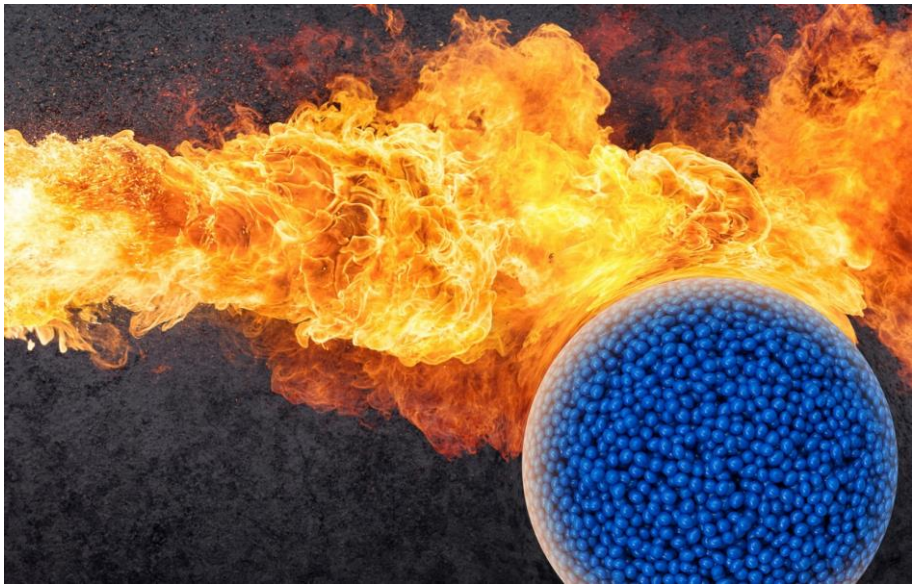
Appendix 4. (Image: © 2019 KRAIBURG TPE)



Appendix 5. (Image: © 2019 KRAIBURG TPE)

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About KRAIBURG TPE

KRAIBURG TPE (www.kraiburg-tpe.com) is a global manufacturer of thermoplastic elastomers. From its beginning in 2001 as a subsidiary of the historical KRAIBURG Group founded in 1947, KRAIBURG TPE has pioneered in TPE compounds, today being the competence leader in this industry. With production sites in Germany, the U.S., and Malaysia, the company offers a broad range of compounds for applications in the automotive, industrial, consumer, and strictly regulated medical sectors. The established THERMOLAST®, COPEC®, HIPEX®, and For Tec E® product lines are processed by injection molding or extrusion and provide numerous processing and product design advantages to manufacturers. KRAIBURG TPE features innovative capabilities as well as true global customer orientation, customized product solutions and reliable service. The company is certified to ISO 50001 at its headquarters in Germany and holds ISO 9001 and ISO 14001 certifications at all global sites. In 2018, KRAIBURG TPE, with 640 employees worldwide, generated sales of 189 million euros.

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