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High-Performance Fibres – A Review of Properties and IR-Spectra

Visokozmogljiva vlakna – pregled lastnosti in IR-spektrov

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Abstract

High-performance fibres are fibre materials that exhibit at least one extraordinary property compared to conventional fibre materials. That extraordinary property is frequently related to excellent fibre stability against certain influences such as fire, heat, chemicals or light. Also, a high mechanical strength is often a property of high-performance fibres. Nevertheless, it should be noted that high-performance fibres exhibit certain weaknesses in addition to their advantages. This review presents a broad overview of the most important high-performance fibres, with a special emphasis on their chemical structure and related infrared spectra (IR-spectra). The categorization of the fibres according to chemical substance classes was performed to make it easy for the reader to find a fibre of interest. The main categories are polyethylene (PE) fibres, polyacrylonitrile (PAN) fibres, polyvinylalcohol (PVAL) fibres, polyester-based fibres, polyamide-based fibres, polyetheretherketone (PEEK) fibres, polyimide (PI) fibres, halogen-containing fibres, polyphenylene sulfide (PPS fibres), resin-based fibres and finally inorganic fibres. Competing materials are also discussed, and structural related materials can be easily identified. In addition to discussing fibre properties and selected applications, one of the main aims is to present a various number of IR-spectra as a tool for structural understanding and to help identify unknown fibres. Here, beside the IR-spectra of high-performance fibres, the reference IR-spectra of common fibres are presented for comparison.

Keywords: High-performance fibres, synthetic fibres, inorganic fibres, infrared spectroscopy

Izvleček

Visokozmogljiva vlakna so vlaknine, ki imajo v primerjavi s konvencionalnimi vlakninami vsaj eno izjemno lastnost. Izjemne lastnosti so pogosto povezane z odlično stabilnostjo vlakna pri nekaterih vplivih, kot so ogenj, toplota, kemikalije ali svetloba. Tudi visoka mehanska trdnost je pogosta lastnost visokozmogljivih vlaken. Kljub temu je treba upoštevati, da imajo visokozmogljiva vlakna poleg svojih prednosti tudi nekatere neprijetne slabosti. Članek podaja širši pregled najpomembnejših visokozmogljivih vlaken s posebnim poudarkom na kemični strukturi in z njo povezanih infrardečih spektrih (IR-spektri) vlaken. Vlakna so predstavljena v skupinah glede na njihovo kemično razvrstitev, tako da bralec laže najde vlakno, ki ga zanima. Glavne skupine so polietilenska vlakna, poliakrilonitrilna vlakna, polivinilalkoholna vlakna, vlakna na osnovi poliestrov in poliamidov, polietereterketonska vlakna, poliimidna vlakna, vlakna, ki vsebujejo halogene elemente, polietilensulfidna vlakna, vlakna na osnovi smole in na koncu anorganska vlakna. Prav tako so obravnavane konkurenčne vlaknine in tudi strukturno sorodnih vlaknin ni težko razpoznati. Poleg lastnosti vlaken in izbranih področij uporabe je glavni cilj predstaviti številne IR-spektre kot orodje za strukturno razumevanje, pa tudi kot pomoč pri razpoznavanju neznanih vlaken. Tu so poleg IR-spektrov visokozmogljivih vlaken za primerjavo podani tudi referenčni IR-spektri tekstilnih vlaken.

Ključne besede: visokozmogljiva vlakna, sintetična vlakna, anorganska vlakna, infrardeča spektroskopija

1 Introduction

High-performance fibres are fibres with at least one outstanding property, i.e. a high-performance property. Beside a high mechanical strength, this high-performance property is often related to the high stability of the fibres against various influences such as heat, fire, chemicals, light, etc. [1-4]. However, each high-performance fibre has specific disadvantageous properties in addition to its advantageous high-performance property [4]. The best example to explain this issue is probably Kevlar fibre based on the polymer para-aramid. This fibre has a high strength and excellent flame-retardant property, but contains a very low light stability [5, 6].

The fields of application of high-performance fibres relate to their outstanding properties. In fields where these properties are demanded, these high-performance fibres are used. Fibres with high mechanical strength are used, for example, for the production of ropes, cut-resistant textiles and bullet-proof vests [7, 8]. They also find applications in fibre-reinforced composite materials [9]. Non-flammable fibres find applications, for example, in fire-protective clothes and in airplane interior textile materials [10, 11]. Fibres with excellent stability against heat and chemicals can be also be used for the production of protective clothes [12]. However, they are frequently used as filter materials for hot and aggressive gases.

The aim of this review is to give an overview regarding the most important high-performance and innovative fibres on the market. Some advantageous and disadvantageous properties are discussed in relation to the chemical structure of the polymers used to build up these fibres. Related to the chemical structure is the infrared spectrum, which enables the identification of specific functional chemical groups. The vibration of a chemical bond can be stimulated through the absorption of infrared light containing a specific energy. This specific energy corresponds to a certain wavelength of the infrared light. Beside using energy or wavelength, infrared spectra are usually shown in the function of wavenumber using the unit cm⁻¹. This wavenumber is a reciprocal unit of the wavelength. A prominent example from the field of textile can be given with acrylic fibres. Acrylic fibres contain the nitrile group -CN, which contains a carbon-nitrogen triple bond. The stretching vibration of this carbon-nitrogen triple bond can be stimulated by infrared light in the wavenumber range of 2,240 cm⁻¹ to 2,260 cm⁻¹ [13, 14]. An infrared signal in this range of wavenumbers is guite unique for polyacrylonitrile. For this, acrylic fibres can be easily identified and distinguished from other fibres using IR-spectroscopy. In addition to the identification of specific chemical groups, IRspectroscopy can be used to identify chemical compounds by comparison with spectra from literature or databases. Here, the spectral range from 600 cm⁻¹ to 1,750 cm⁻¹, in particular, is compared. For this, this spectral range is also called the fingerprint area [13]. IR spectroscopy is an appropriate method for the quick identification of high-performance fibres without the need for sample destruction. Such a quick identification is often demanded in production processes to verify materials used. The identification of materials is also required during recycling of polymers and fibres.

In this review, fibres with similarities in the chemical structure are classified into the same category and described in the related sub-chapters. Competing fibre materials are named. as well as some advantageous and disadvantageous properties. The chemical structures of fibres are depicted and discussed according to some fibre properties, but also in relation to the recorded IR-spectra. All IRspectra shown are exclusively measured for presentation in this review paper. For some fibre materials, the same fibre types from different products used in different applications are measured and compared. Instead of the fibre products, related bulk materials are examined using IR-spectroscopy for other fibres. One main reason for these alternative measurements is that several high-performance fibres are only available as compositions in blended yarns and fabrics. High-performance fibres are often quite expensive and, in the best-case scenario, their application in a small amount can lead to new and innovative products.

2 Parameters for description of fibre properties

The parameters to describe fibre properties can be put into several categories related to the area of interest. It is quite useful to use the following four categories: mechanical properties, temperature/flame stability, chemical stability and light stability. Mechanical properties used for fibre description include elastic modulus, tensile strength or elongation at break. For the description of the temperature stability of fibres, the values for glass temperature (T_c) , melting temperature (T_{M}) and the temperature of decomposition (T_p) are suitable. In addition, the maximum temperature of usage (T_{max}) is quite frequently recommended by the supplier of a fibre. An overview of T_{max} values for a broad range of different fibres is given in Table 1. It is clear that there is a certain range of variation for each temperature value, even for the same type of fibre. This variation can be explained by different properties, even if the fibre is built up by the same type of polymer (e.g. different grade of crystallization, degree of polymerization, additives or co-polymer units). Also, the type of method for determining these values can have a certain influence, i.e. measuring the decomposition temperature under air or inert gas. In the case of T_{max} , the type of usage is also of relevance. The flame-retardant properties of a fibre material are usually described by the LOI (limited oxygen index) value. An overview of several LOI values is also given in Table 1. This value indicates the amount of oxygen that is necessary to set a fibre material on fire. Increasing LOI values also improves the flame-retardant properties of a fibre. Fibres with a low LOI of less than 21% can be easily ignited.

The description of the chemical stability of a fibre is almost more challenging and is determined through investigations comprising two parts. The first part is the influence of the chemical of interest on a fibre. Here, many process variations are possible, such as temperature, duration of contact or concentration. The second part is the fibre property that is measured before and after the chemical treatment, i.e. measuring the weight of the fibre material or its tensile strength. In a certain way, the testing of light stability of fibres is similar. Here, a certain fibre property is tested before and after illumination with light and is compared to reference materials. In combination with UV-stability, light stability is often called sun light stability or weathering stability. It should be clear from this overview that the light stability of a fibre strongly depends on the type of light that is used for illumination and other surrounding parameters such as humidity or temperature.

Given this broad range of different parameters for describing high-performance fibre properties, the limitation of this review paper is clear. Only the most important points can be mentioned for each presented fibre.

3 Materials and methods

All infrared spectra presented in this review were measured especially for this paper. These measurements were performed using a IR Prestige 21 spectrometer supplied by Shimadzu, together with a Specac Golden Gate ATR unit. The fibre samples were taken from different sources and were tested as received without further treatments. Particularly worthy of mention are non-woven filter materials from the companies BWF Offermann, Waldenfels & Co (Offingen, Germany) and Zhejiang Rayjet Filter Media Technology (China). Several types of glass and silica fibres were obtained from Culimeta Textilglas Technologie GmbH (Bersenbrück, Germany). Sieve fabrics made from halogenated fibres were supplied by Reichelt Chemietechnik GmbH (Heidelberg, Germany). Several ropes and lines were obtained from the company Hamburger Tauwerk Fabrik (Hamburg, Germany). Polyethylene fibre non-woven, as reference material, was supplied by Modulor GmbH (Berlin, Germany). Several protein fibre materials used as reference materials were obtained from the company Das Wollschaf (Zweibrücken, Germany). Flame-retardant polyester and water-soluble yarns and fibre felt made from polyvinylalcohol fibres were obtained from the company StoffeDE (Schenefeld, Germany). Different fibre and polymer materials were obtained from Goodfellow GmbH (Friedberg, Germany). For some high-performance fibres, it was only possible to obtain this fibre in blended yarns and fabrics. In these cases, the IR-spectra were taken from the pure polymers supplied in other forms, such as plate, foil or bullet.

4 Synthetic fibres

Synthetic fibres are often referred to as chemical fibres and, by this distinguished form, natural fibres.

Table 1: Overview of the properties of several fibre materials (conventional and high-performance). Compared are the maximum temperatures for continuous usage, the LOI value and a selection of some properties that are typical for this type of fibre. The different mentioned values are compared from different reference sources. Some important brand names are given in brackets.

Type of fibre	Maximum temperature of usage (°C)	LOI (%)	Selected properties	References
Cellulosics	80	17	High humidity up-take	[15, 16]
Polypropylene PP	90	17	High chemical stability	[15, 17]
Polyethylene HPPE, (Dyneema)	90	18	High strength, high elastic modulus	[15, 18]
Wool	94	25	High humidity up-take	[15, 19]
Polyamide PA	110/115	24 (Nylon)	Mechanically stable, stable against abrasion	[15, 20]
Polyacrylonitrile PAN	125	18 (homo- PAN)	Stable against hydrolysis, light, weathering	[15, 21]
Polyester PET	150	21	Low cost	[15, 22]
Phenolic resin, novolac resin (Kynol)	150/200	30-34	Resistant against heat and fire	[15]
Polyetherimid, PEI	170	44	Resistant against heat and fire	[21]
Polyamidimid, PAI (Kermel)	180/200	30-32	Good temperature stability	[15]
Polyimid, PI (P84)	180/260	36/38	Good mechanical and thermal properties	[15, 23]
Polyphenylenesulfide PPS	190/200/280	40	Good chemical and thermal stability	[15, 23]
Meta-aramid (Nomex)	200	30-32	Good temperature stability	[15, 23]
Preoxidized PAN (Panox)	200	50	Good temperature stability, flame-retardant	[15]
Para-aramid (Kevlar)	190/200	28-30	Extraordinary mechanical properties, stability against contact heat	[15, 23]
Polyetheretherketone, PEEK	250	28/35	High temperature materials	[21, 23]
Polytetrafluoroethylene PTFE	250/260	95	Extraordinary chemical stability	[15, 23]
Polybenzimidazol, PBI	250/300	40/41	Extraordinary thermal stability	[15, 23]
Phenylene Benzobisoxazol, PBO (Zylon)	310/350	56-68	Extraordinary mechanical properties, stability against contact heat	[15, 21, 23]

Synthetic fibres are also referred to as organic fibres and, by this distinguished form, inorganic fibres. If synthetic fibres are referred to as man-made fibres, they are, by this distinguished form, natural fibres. Below, synthetic fibres with high-performance properties are summarized and categorized for this purpose into groups related to their chemical composition. Later, in section 5, some inorganic high-performance fibres are presented.

4.1 Polyethylene, PE

Polyethylene PE is probably one of the most used polymeric materials worldwide. Its chemical structure is the simplest of all synthetic polymers (Scheme 1). PE is used in many products from everyday life. Probably the most prominent PE product is the disposable plastic bag. PE is the first choice for many applications because it is a low-cost material. Nevertheless, there are also high-performance and high-price PE products. High-performance polyethylene fibres (HPPE) are known for their high strength and their low specific weight (low density) [24]. Also, these HPPE fibres have good weathering stability and stability against salt water, which is important for marine applications. Manifold applications of HPPE fibres are found in protective clothing, composites, ropes, cables and in the field of medicine [24]. The many disadvantages of HPPE fibres include their low temperature resistance due to their low glass temperature T_{c} of around 90 °C and their high flammability, which is reflected in a low LOI value of around 18 [18]. It is also quite difficult to modify polyethylene fibres through chemical finishing because there are no functional groups on the fibre surface that could interact with the anchor groups of finishing agents [26]. The chemical structure of HPPE is the same as the structure of conventional polyethylene, if the structure of the monomer unit is considered (see Scheme 1). The main difference is the molecular weight, which is very high for HPPE, with values above one million g/mol. For this reason, the name UHMW-PE is used (ultrahigh molecular weight -PE) in addition to HPPE. For UHMW-PE, a molecular weight of more than 1 million g/mol means a polymerization degree in excess of 35,000. In comparison, conventional PE has a significantly lower molecular weight. For HDPE (high density polyethylene) materials, a molecular weight in the range of 100,000 g/mol is typical. LDPE (low density polyethylene) materials exhibit an even lower molecular weight and contain a branched polymeric structure that also contains side chains [27]. Several years ago, two companies were the main suppliers of HPPE fibres: DSM (Netherlands), with the brand Dyneema fibres, and Honeywell (USA) with the brand Spectra fibres. For this reason, often the name "Dyneema"

is typically used as synonym for HPPE fibres [2]. Nevertheless, there are many competing companies today that offer different types of HPPE fibres. The IR-spectrum of polyethylene is quite simple due to the simple chemical structure of this polymer (Figure 1). Only four main signals dominate the IRspectrum of polyethylene. These signals are related to the stretching and deformation vibration of the C-H bonds and -CH₂- units that build up this polymer [13]. It is not possible to distinguish HPPE fibres from conventional PE materials using IR spectroscopy because their monomer units are chemically identical (Figure 1). One of the main applications of HPPE fibres are highstrength, light- weight ropes. For this reason, samples from ropes based on HPPE fibres were also taken and their IR-spectra were recorded (see comparison in Figure 1). One rope is a two-component system with a core made from grey-coloured Dyneema fibres and a braided surface made from PBO fibres. The other rope is made from high molecular weight polyethylene (HMPE), which contains an undefined black coloration. The both spectra of these commercial HPPE ropes exhibit the four main signals that can be attributed to the polyethylene structure. However, significant additional signals can be identified. The signal at 1,726 cm⁻¹ or 1,728 cm⁻¹ is typically attributed to a C=O stretching vibration, which of course cannot be caused by the polyethylene itself [13]. These HPPE ropes are probably modified or coated to improve their properties, i.e. to improve flame-retardant properties.





Scheme 1: Chemical structure of polyethylene (PE)



Figure 1: IR-spectra of two different fibre materials made from polyethylene (PE) (left) and IR-spectra of commercially available ropes based on HPPE (right)

4.2 Polyacrylonitrile, PAN

Polyacrylonitrile (PAN) is the polymer used for the production of acrylic fibres. Besides polyester and polyamide fibres, acrylic fibres are the third important conventional chemical fibre and are used for a broad range of garments. In addition to this use for conventional clothing purposes, PAN fibres are also used as technical fibres, in particular because of their strength, their high stability against chemicals, and their light and weathering properties [28]. Applications include sun shades, tents or as filter materials [21, 28]. PAN fibres from high molecular weight polyacrylonitrile (UHMW-PAN) are used for the production of carbon fibres [29]. One disadvantage of PAN fibres is their high flammability as indicated by a LOI value of 17 (see Table 1) [20]. The chemical structure of polyacrylonitrile is shown in Scheme 2. The structure shown is a homopolymer, which is only built up by one type of monomer unit (the acrylonitrile unit). The main technical application of fibres from homopolymer PAN find is as filter materials for the filtration of hot and aggressive gases. In contrast, conventionally used acrylic fibres are not made from homopolymer PAN. In addition to an acrylonitrile monomer unit, they also contain other building units, up to a ratio of 50%. Fibres made from these copolymers are also referred to as acrylics or modacrylic fibres depending on the ratio of the co-unit. They are used in the garment industry. Copolymers of PAN are also used as filters for technical purposes [15].

The IR-spectra of a PAN homopolymer and PAN copolymer are compared in Figure 2. Both samples are taken from non-woven materials used for filtration purposes. Besides the C-H stretching vibration, the IR-spectra also indicate the signal at 2,241 cm⁻¹, which is attributed to the stretching vibration of the CN triple bond. An IR-signal in this range of the spectrum is quite unique for fibre materials and can be used for the simple detection of PAN fibres [13, 30]. The finger print areas of both spectra are clearly different (Figure 2). The spectrum of the PAN copolymer shows a strong signal at 1,735 cm⁻¹ and an additional peak at 1,635 cm⁻¹. These signals could be the result of the co-unit in the copolymer. The signal at 1,735 cm⁻¹ is probably caused by a C=O stretching vibration, which could, for example, be part of an ester group in a co-monomer unit. The signal at 1,635 cm⁻¹ can be attributed to the solvent dimethylformamide (DMF). DMF is frequently used in wet spinning processes for PAN fibre production and can remain as an impurity in PAN fibres after the spinning process. DMF is an amide and exhibits a C=O stretching vibration in its IR-spectrum typical for amides in the spectral range of around 1,630 cm⁻¹ [31, 32].



Scheme 2: Chemical structure of polyacrylonitrile (PAN) (homopolymer)



Figure 2: Two IR-spectra of polyacrylonitrile (PAN). Comparison of PAN homopolymer and PAN copolymer; both materials are used as non-woven for filter applications.

4.3 Polyvinylalcohol, PVAL

Similar to PAN fibres, polyvinylalcohol fibres (PVAL) also exhibit a certain strength and stability against different chemicals [33]. Similar to PAN fibres, PVAL is represented by a simple chemical structure. In most cases, however, PVAL fibres are built up by a copolymer (see Scheme 3). Depending on the composition of the copolymer, a distinction must be made between water-insoluble and water-soluble PVAL fibres. Moreover, water-soluble types are distinguished by the temperature of water, which is necessary to produce the fibres. The copolymeric structure of PVAL fibres is the result of the production process of this polymer. Monomer yinylacetate is initially polymerized into polyvinylacetate. In the second step, re-esterification is performed and alcohol groups are formed in the polymer chain. Finally, the degree of re-esterification determines the ratio of both types of monomer units shown in Scheme 3.

Applications of water-soluble PVAL fibres include water-soluble sewing yarns or fibre felts, where removal after the production process is desired. PVAL sewing yarns are also used in the medical field. These medical sewing yarns have the ability to decompose after a wound is healed and the yarn is no longer needed. Water-insoluble PVAL fibres find applications in the garment industry, where the chemical and mechanical stability of products are required. Also, a modified flame-retardant PVAL fibre was presented at the TechTextil 2019 fair in Frankfurt (Germany) and is supplied under the brand name Vinaryl. The supplier of this flame-retardant fibre product emphasizes chemical stability against acids and alkali relative to the lower stability of other FR fibres, such as aramid or FR-rayon.

The IR-spectra of two different water-soluble PVAL fibre products are compared in Figure 3. A sewing yarn and a fibre felt are compared. The IR-spectra of both materials have nearly the same shape. However, the maxima of some signals appear at different wave-numbers. The IR-spectrum of a water-soluble PVAL sewing yarn exhibits strong signals at 3,339 cm⁻¹ and 2,909 cm⁻¹. These signals are related to O-H and C-H stretching vibrations, respectively. The strongest signal at 1,085 cm⁻¹ is attributed to the C=O stretching vibration. A signal at 1,726 cm⁻¹ can be attributed to a C=O stretching vibration [13]. This C=O bond is



Scheme 3: Chemical structure of polyvinyl alcohol (PVAL) with a co-monomer unit of vinylacetate



Figure 3: IR-spectra of two water-soluble fibre materials made from polyvinylalcohol. A sewing yarn and a fibre felt are compared.

probably part of the acetyl group of the comonomer unit in the PVAL structure.

4.4 Polyesters and related materials 4.4.1 Polyester types

Polyesters are generally polymers in which monomer units are connected by ester groups. An overview of some polyester types and their main properties is given in Table 2, in which a comparison with polyetheretherketone (PEEK) is also given. Polyethylene terephthalate (PET), as the most prominent polyester, enjoys the highest global market share in terms of the production of synthetic fibres [1]. Beside conventional PET fibres, there are several other types of polyester fibres with special, high-performance properties. An overview of some examples is given in Scheme 4. The polyester type with a structure most similar to PET is polybutylene terephthalate (PBT). In the case of PBT, the ethylene unit is replaced by a longer butylene unit. Because of this structural difference, fibres from PBT contain a higher elongation at break and higher flexibility than conventional PET fibres.

Polylactic acid (PLA) is a biobased aliphatic polyester because the monomer unit lactic acid is produced through the fermentation of starch. From this it follows that PLA is usually produced through the ring-opening polymerization of the cyclic dimer of lactic acid [34–36]. PLA fibres are biodegradable and bioresorbable. Compared to PET fibres, this is a major advantage for fibre applications where a limited life-time is required. A prominent example is sewing yarn used in the medical sector, where the yarn must be degraded after a wound is completely healed [37]. However, PLA fibres are less biodegradable than natural fibres or fibres made from regenerated cellulose or protein.

High-performance materials with advanced properties include polyesters that are built up by two monomer units, both with an aromatic structure. An example of an aromatic polyester is shown in Scheme 4. Fibres from this aromatic polyester are distributed under the tradename Vectran. These fibres exhibit significantly higher thermal stability and stronger flame-retardant properties than conventional PET (see Table 2). Also, due to the aromatic nature of the polymer chain, aromatic polyester is a stiff polymer rod that is, in some ways similar, to para-aramid. For this, high strength materials are produced from Vectran fibres, including ropes and lines [38].

The IR-spectra of both PET and PBT polyester fibre materials are compared in Figure 4. The strong signals at 1,713 cm⁻¹ and 1,240 cm⁻¹ are related to

Polymer type	Glass temperature T _G (°C)	Melting temperature T_{M} (°C)	LOI	Comments regarding selected properties	References
PET	74/80-85	253–260	21	Low cost, conventional polyester	[21, 22, 39–41]
РВТ	20-40/ 47-52	212–220/ 221–226	20	Higher elasticity	[41-45]
PLA	54	170-175	20	Bio-based	[21, 46, 47]
Vectran; aromatic polyester	At 260 loss of crystal order	350	28/30	Rigid-rod polymer	[48-50]
PEEK	146–157	334	28/35	Thermal stability	[21, 23, 51]

Table 2: Overview of some properties of different types of polyester and polyetheretherketone (PEEK). $T_{_{G'}} T_{_{M}}$ and LOI values, as reported from different literature sources, are compared.



Scheme 4: Chemical structures of different polyester types used for fibre production

the ester groups with the stretching vibration of the C=O bond and the C-O-C unit. The weak signal at 2,968 cm⁻¹ is in line with the C-H stretching vibration [52]. All main signals of both materials occur at the same positions in the spectra. Because of the similar structure of both polyester types, the shape of their IR-spectra is nearly the same. Only in the fingerprint area, a few small features appear that are different.

As compared in Figure 4, the IR-spectrum of a flame-retardant polyester (from PET) is also presented. This material is supplied under the tradename Trevira FR and its flame-retardant properties are, according to supplier information, based in part on the phosphorous component, which is part of the polymer structure [53]. The IR-spectrum of this flame-retardant polyester is nearly the same as the spectrum of PET. The wavenumbers differ by only a few signals in a small range. Here, it can be stated that it is not possible to identify the flame-retardant component using IR-spectroscopy.



Figure 4: IR-spectra of two different polyester fibre materials made from polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) (left) and the IR-spectrum of the commercially available fire-retardant polyester Trevira (right)

The spectra of the other two polyester fibre materials (PLA and Vectran) are presented in Figure 5. Both spectra are dominated by the strong signal related to the stretching vibration of the C=O double bond. For the PLA fibres, the C=O signal is detected at 1,748 cm⁻¹, while this signal for the Vectra fibre occurs at a lower wavenumber of 1,726 cm⁻¹ [54, 55]. This appearance at a smaller wavenumber may be related to a weaker C=O bond in the Vectra fibre relative to the stronger C=O bond in PLA. The C=O bond is probably weakened due to the delocalization of the binding electrons of the C=O double bond in the attached aromatic ring systems. In contrast, no delocalization of bonding electron is possible in the aliphatic polyester PLA. In the IR-spectrum of PLA, the strongest signal appears at 1,086 cm⁻¹, which is attributed to the stretching vibration of the C-O-C unit [55]. For both fibre types (PLA and Vectran), the signals according to the C-H stretching vibration are weak. For PLA fibres, these signals appear at 2,947 cm⁻¹ and 2,997 cm⁻¹. The appearance of these signals in a range below the wavenumber of 3,000 cm⁻¹ is typical for C-H units, which are part of the aliphatic structure. In contrast, the signal of Vectran appears at 3,071 cm⁻¹. This position in a range higher 3,000 cm⁻¹ is typical for a C-H unit that is part of an aromatic ring system.

For comparison purposes, the IR-spectrum of commercially available Vectran rope is also shown in Figure 5. To protect Vectran fibres in the rope, a block coating is present on the rope's surface. This coating should protect the Vectran against mechanical influences, but probably more important is protection against light and weathering. Vectran exhibits an aromatic polymer structure with a large conjugated aromatic system. For this reason, it has the ability to take up UV-light easily and is this resistant to decomposition by sun light.

The IR-spectrum of the Vectran rope exhibits the same main signals at 1,726 cm⁻¹ and 1,233 cm⁻¹ as the other Vectran sample. The most prominent difference is the appearance of signals at 2,851 cm⁻¹ and 2,918 cm⁻¹, which are probably related to the C-H stretching vibration of the aliphatic components. The broad signal at 3,312 cm⁻¹ could be attributed to a stretching vibration of an O-H bond or a N-H bond. From this it can be assumed that the black coating on the surface of the Vectran rope is based on Nylon.

4.4.2 Polyetheretherketone (PEEK)

Fibres produced from polymer polyetheretherketone (PEEK) can be referred to as polyester-related material, even if the chemical structure of PEEK does not contain any ester group (Scheme 5). The properties and applications of PEEK fibres are quite similar to those of conventional PET fibres. However, due to its higher glass and melting temperature, the maximum temperature of usage of PEEK fibres is nearly 100 °C higher than that of PET fibres (see Tables 1 and 2) [23, 51]. For this reason, PEEK fibres are thermally more stable and flame-retardant than PET fibres. Also, the chemical stability against acids and alkaline solutions of PEEK fibres is better than that of PET fibres because of the stronger hydrolysis stability of ether groups in PEEK fibres relative to the ester groups of PET fibres. Besides PEEK, there are also other types of polyether ketones with different chemical structures, depending on the different number of keto- and ether-groups in the repeating unit of the polymer. The chemical structure of PEEK is shown



Figure 5: IR-spectra of two different polyester fibre materials made from an aromatic polyester supplied under the brand name Vectra and polylacticacid (PLA) (left) and the IR-spectrum of a commercially available Vectran rope (right)

in Scheme 5, and contains three benzene rings, two ether groups and one keto group in each repeating unit.

The IR-spectrum of PEEK is recorded from a PEEK monofilament (Figure 6). The weak signal at 3,067 cm⁻¹ is related to the C-H stretching vibration of C-H as part of the aromatic ring systems.

The signal at 1,654 cm⁻¹ is attributed to the C=O stretching vibration of the keto group. Signals at 1,489 cm⁻¹ and 1,593 cm⁻¹ can be attributed to the C=C vibration in the aromatic ring system. The strong vibration at 1,223 cm⁻¹ is related to the C=O stretching vibrations in the ether group [56]. The signal at 833 cm⁻¹ can be attributed to C-H vibration of two neighbouring hydrogen atoms that are placed at the benzene ring. This position and signal are typical for benzene rings with a 1.4 substitution [13].



Scheme 5: Chemical structure of polyetheretherketone (*PEEK*)



Figure 6: IR-spectrum of polyetheretherketone (PEEK)

4.5 Polyamides and related materials

4.5.1 Polyamide types

Polyamides are polymers in which monomer units are connected by amide groups. The chemical structure of three prominent polyamides is depicted in Scheme 6. Shown is the polyamide 6.6, PA6.6, as an example of an aliphatic polyamide. PA6.6 is also distributed as a conventional fibre under the name Nylon. Para-aramid and meta-aramid are shown as examples of aromatic polyamides. The related fibre products are distributed under different tradenames, including Kevlar and Twaron for para-aramid, and Nomex for meta-aramid.

Polyamide 6.6 is built up by two monomer units, each containing six carbon atoms. Also available on the market are aliphatic polyamides with larger monomer units, including polyamide 6.10 or polyamide 10.10. Products in this area are supplied, for example, under the tradename Vestamid by Evonik. Besides other properties, fibres made from these special polyamides demonstrate higher flexibility, lower water up-take, better chemical resistance and lower melting points than conventional PA6.6 fibres. [57].

Aromatic polyamides such as para-aramid or meta-aramid are high-performance fibres with flame-retardant properties and LOI values in the range of 28 to 32 (see Table 1) [23]. Para-aramid is built up using rigid polymer rods. These rods are strongly connected with each other by hydrogen bridge bonds. As a result of this structure, fibres from para-aramid exhibit high strength and are used, for example, in ballistic protective textiles, high strength ropes or as reinforcement fibre in composite materials [23]. Meta-aramid has a lower strength than para-aramid, and is used for applications where a good chemical resistance is required [23]. There are also polyamides on the market containing an aromatic and an aliphatic monomer unit, such as the PA9T fibre supplied by Kuraray [58].

The IR-spectra of polyamide 6.6 and both the aromatic polyamides para-aramid and meta-aramid are compared in Figure 7. These spectra are dominated by signals typical for amide groups. The N-H stretching vibration is related to a signal at around 3,300 cm⁻¹. Further, the amide groups are related to several signals in the IR-spectra, referred to as Amid I, Amid II and Amid III [14]. The Amid I signal is caused by the C=O stretching vibration of the C=O double bond in the amide group. Amide II is attributed to a combination of the stretching vibration of the C-N bond and a deformation vibration of the C-N-H unit [53]. Some publications assign a second signal of around 3,086 cm⁻¹ according to the overtone of the Amid II vibration [14].

For para-aramid, the Amid II signal at 1,537 cm⁻¹ appears as a double peak related to the C-N stretching vibration and N-H bending vibration [59]. For secondary amides, the weak Amide III signal in the range from 1,200 to 1,330 cm⁻¹ can also be attributed for polyamides. This Amide III signal is caused by a combination of the deformation vibrations from the N-H and OCN groups [14]. For PA6.6 fibres, the sig-

nals attributed to C-H stretching vibrations are of average intensity. The signals from the C-H stretching vibration are very weak compared to para-aramid and meta-aramid. For para-aramid, the signal at 820 cm⁻¹ can be attributed to the C-H deformation vibration of the two neighbouring hydrogen atoms that are placed at the benzene ring. This position and signal are typical for a benzene ring with a 1.4 substitution [61]. Analogously for meta-aramid, the signal at 779 cm⁻¹ can be attributed to the C-H deformation vibrations typical for a 1.3 substitution at the benzene ring [13].



Scheme 6: Chemical structures of polyamide 6.6, PA 6.6 (Nylon), para-aramid and meta-aramid



Figure 7: IR-spectra of three different polyamide fibre materials made from polyamide 6.6, para-aramid and meta-aramid

4.5.2 Protein-based regenerated fibres

Similar to synthetic polyamides, protein-based fibres are also built up by polymers, in which monomer units are connected by amide groups. In contrast to synthetic polyamides, however, the monomer units of proteins are amino acids. Protein fibres are mainly animal fibres such wool or silk. It is also possible to produce regenerated protein fibres from proteins of different sources such as soya (plant source) or casein from milk (animal source). The development of such protein-based regenerated fibres is quite old and even reported in patents from the 1940s [62, 63]. Today, particularly "milk fibre" is promoted as a kind of sustainable alternative fibre [64]. However, soya fibre has also made a comeback in recent years [41]. A recent and very innovative approach is the use of the biotechnological production of spider silk proteins for fibre production. These spider silk fibres exhibit a significantly higher elasticity than conventional silk fibres [65].

The IR-spectra of two different types of regenerated protein fibres are compared in Figure 8 using the IR-spectrum of mulberry silk as a reference for a natural fibre. The prominent signals related to the N-H stretching vibration and for Amid I and Amid II can be clearly identified for all three types of fibres, even if the signals appear at different positions on the spectra. The IR-spectra of these protein fibres exhibit the same main features as the spectra of the synthetic polyamides (compare Figures 7 and 8). Completely different are the compared IR-spectra of protein fibres in the fingerprint range below 1,400 cm⁻¹. This difference is related to the different composition of these protein fibres. These protein fibres are built up using different combinations of amino acids containing different functional groups. Silk protein is known to contain a high ratio of the simplest natural amino acid glycine. In contrast, casein and proteins from soya are built up using a higher variety of different natural amino acids [66].



Figure 8: IR-spectra of three different protein-based fibre materials: mulberry silk and regenerated fibres from soya and milk proteins

4.5.3 Polyamide-imide, PAI & Polyimide, PI

Polyimides (PI) are polymers in which monomer units are connected by imide groups. The structure of one commercially available polyimide is presented in Scheme 7. This polyimide is used for the production of high-performance fibres with excellent temperature stability. The maximum continuous working temperature is reported at 260 °C [67]. For this reason, the thermal stability is in the same range as that of PTFE fibres. Applications for polyimide fibres are found in filter materials for hot gases. The flame-retardant properties of polyimide fibres are also excellent. Thus, polyimide fibres are used in blended fabrics for fire-retardant clothes. Of course, there are different types and chemical structures possible for polyimides. One very prominent example is the polyimide shown in Scheme 7, which is also distributed under the tradename P84 [67]. Polyamide-imides (PAI) are polymers in which monomer units are connected by amide groups and imide groups. Some authors categorize polyamide-imide fibres to aramid fibres, in particular to meta-aramid because of some similarities in the structure. However, there is a significant chemical difference between meta-aramid and fibres from polyamide-imide, i.e. the presence of the imide group in PAI fibres. The structure of a polyamide-imide, which is used for production of a commercially available fibre, is presented in Scheme 7. This fibre is also distributed under the tradename Kermel and is promoted in particular for its flame-retardant properties [68]. Products are found often with blended fabrics, such as flame-protective underwear and workwear.

The IR-spectrum of polyimide fibres from type P84 is shown in Figure 9. This IR-spectrum from polyimide fibre is compared to the spectrum from polyamide-imide taken from a bulk sample. The spectrum of polyimide fibre is dominated by a strong signal at 1,715 cm⁻¹, which is related to the stretching vibration of a C=O double bond. A second signal at 1,776 cm⁻¹ can also be attributed to the stretching vibration of a C=O bond. In fact, the structure of P84 exhibits two different types of C=O groups in the monomer unit (see Scheme 7). One C=O bond is part of a keto group, while the other four C=O bonds are parts of the imide groups. This explains the appearance of two signals for two different types of C=O bonds. Another explanation of these two signals is the assignment to the two different vibrations (symmetric and asymmetric) of the imide group. Imides, as part of five-membered aromatic rings, have been found to exhibit two signals around 1,700 cm⁻¹ and 1,770 cm⁻¹ [13]. Both of these signals relate to the symmetric and asymmetric stretching

vibrations of the two C=O bonds of the same imide group. Also, the IR-spectrum of polyamide-imide exhibits two signals at 1,709 cm⁻¹ and 1,776 cm⁻¹, which can be attributed to the stretching vibrations of C=O bonds as part of the imide group, similar to the spectrum of polyimide. The signal for the C=O stretching vibration of the amide group usually appears at a lower wavenumber, while the signal at 1,658 cm⁻¹ can probably be attributed to the amide group. In contrast, the C-H stretching vibrations lead only to weak signals in the IRspectrum of the polyimide P84. The signal at 3,057 cm⁻¹ can be attributed to the C-H vibration of H-atoms bonded to the aromatic ring systems. The other signal at 2,924 cm⁻¹ can be attributed to the C-H vibration of H-atoms that are part of the -CH₂- unit. The signal at 718 cm⁻¹ can be attributed to the deformation vibration of the -CH₂- unit. For the polyamide-imide sample, only a very weak signal at 2,924 cm⁻¹ can be identified, and can be attributed to the C-H stretching vibration.



Scheme 7: Chemical structures of a polyamide-imide (PAI) and a polyimide (PI). These types of polymers are used for fibre production. The PAI shown is distributed as a fibre under the tradename Kermel. The PI shown is distributed as a fibre material under the tradename P84 by the European company Evonik.



Figure 9: IR-spectra of the polyimide fibre P84 and a polyamide-imide bulk sample

4.5.4 Elastane fibres

Elastane fibres are highly elastic synthetic fibres, and are supplied under the tradenames Lycra and Spandex. Elastane is broadly used in the clothing industry at ratios ranging from around 3 to 5 wt-% to increase the flexibility and the body fitting of garments. Elastane fibres can be referred to as high-performance fibres and as a polyamide-related material. The term high-performance traditionally relates to strong fibre stability against different parameters. In the case of elastane, however, the high-performance property is strong elasticity. The chemical structure of elastane is schematically presented in Scheme 8. This polymer is built up using repeating units containing two parts: a flexible polyethyleneoxide chain of around 40 ethyleneoxide units, and a stiff chain segment built up by connecting several aromatic ring systems and urethane groups [69]. This stiff segment is strongly bonded to the stiff segments of other elastane polymers inside the monofilament by hydrogen bridges. In some ways, this is similar to the attractive interaction between the polymer chains in Nylon or aramid fibres. In contrast, the polyethylene oxide unit forms a random polymer coil without strong attractive bonds to other neighbouring polymer chains. If a mechanical force pulls the polymer, the polymer coil from the polyethylene oxide is easily stretched to a multiple of its size. In this way, the elastane fibre becomes an elongated manifold. This type of elasticity is also referred to as entropic elasticity and is similarly found in natural rubber [70].

Beside these elastane fibres based on polyurethane/ polyethyleneoxide copolymers, other types of elastic polymers and fibre materials have also been invented and discussed. An interesting approach offer polymers containing an inorganic backbone as polysiloxanes or polyphosphazenes [71, 72]. Polyphosphazenes are used in the production of nanofibres related to medical applications, but are also used as elastic polymeric material [73]. Additionally, polyphosphazenes are used for flame-retardant finishing processes [74]. For this reason, they can combine elastic properties with the high-performance property of fire retardance in one fibre material.

Because elastane fibres are only used in small amounts in a mixture with other fibres, it would be advantageous to separate a typical elastane fibre for investigation using IR spectroscopy. There are also different types of elastane fibre on the market, which primarily differ in terms of the construction and composition of the stiff chain segment. For this reason, it is not possible to identify an IR-spectrum that can be referred to a as typical and original IRspectrum of elastane.

Figure 10 presents the IR-spectrum of an elastane monofilament that is used as the core filament of a polyester yarn. This elastane core is removed from the polyester yarn and separately measured to identify, in particular, the IR-spectrum of elastane. The weak and broad signal at 3,323 cm⁻¹ can be attributed to the N-H stretching vibrations of the urethane groups. Three strong signals at 2,801 cm⁻¹, 2,877 cm⁻¹ and 2,936 cm⁻¹ are caused by the stretching vibrations of C-H bonds. However, the strongest signal is observed at 1,105 cm⁻¹. This signal probably relates to the C-O stretching vibration of the ether unit in the polyethylene oxide PEO part of the polymer. Due to the size of the PEO unit, the ether group is the most dominant functional group in the elastane structure. The appearance of this strong signal can be deemed typical for elastane fibres. Other signals in the spectral range from 1,400 cm⁻¹ to 1,732 cm⁻¹ can be attributed to various types of C=O and C=C stretching vibrations that are part of the stiff monomer segment.



Scheme 8: Chemical structure of elastane



Figure 10: IR-spectrum of an elastic filament yarn

4.6 Halogen-containing polymers

Halogen-containing polymers are polymers that contain at least one halogen atom in their monomer unit. Primarily polymers containing the halogens fluorine F and chlorine Cl are used for fibre production. These halogen-containing polymers are not flammable and exhibit LOI values above 34%, depending on the type and number of halogen atoms in the monomer units of the polymers. In the case of thermal decomposition, however, combustion gases with toxic halogen-containing compounds are formed, e.g. HCl or HF. The chemical structure of some fluorinated and chlorinated polymers used for fibre production are shown in Scheme 9. The related IR-spectra are presented in Figures 11 and 12. The most important fluorinated polymer is polytetrafluoroethylene (PTFE), which is fully fluorinated and contains four fluorine atoms for each monomer unit. Due to the strong C-F bond, PTFE exhibits the strongest stability against chemicals among all synthetic fibres. At 95%, its LOI value is also the highest of all organic fibres [23]. The main disadvantages of PTFE are a high-cost factor and the lower strength of fibre material. Another unique feature of PTFE fibre material is its oleophobic property [75]. Polyvinylidene fluoride (PVDF) fibres can be used for the production of filter materials. Moreover, the production of piezoelectric PVDF fibres is also possible, with applications found in smart textiles or E-textiles [76]. Fibre materials from polyvinylidene chloride (PVDC) also exhibit excellent fire-retardant properties. Modacrylic modacrylic fibres with a co-unit of vinylidene chloride are frequently used. These fibres are also supplied under the tradename Kanekalon [77-79].

The IR-spectrum of a non-woven filter material made from PTFE fibres is presented in Figure 11. Due to the simple chemical structure of PTFE, its IR-spectrum exhibits only three significant signals. The strong



Scheme 9: Chemical structures of different chlorine- and fluorine-containing polymers used for fibre production

signals at 1,200 cm⁻¹ and 1,146 cm⁻¹ relate to the C-F stretching vibration, while the signal at 637 cm⁻¹ can probably be attributed to the deformation vibration of the segment $-CF_2$ - [80]. The IR-spectrum of a mono-filament sieve made from ethylene-tetrafluoroeth-ylene-copolymer (ETFE) is also shown in Figure 11 and compared to the spectrum of PTFE. ETFE is a co-polymer with PE and PTFE units. However, the IR-spectrum of ETFE is not a simple combination of the single spectra of PTFE and PE (compare Figures 1 and 11). For ETFE, only a very weak signal at 2,978 cm⁻¹ is identified according to the C-H stretching vibration. Another signal at 1,452 cm⁻¹ relates to the deformation vibration of the segment -CH₂- [81].



Figure 11: Comparison of the IR-spectra of the materials polytetrafluoroethylene (PTFE) and ethylenetetrafluoroethylene-copolymer (ETFE)

IR-spectra of fibre materials from polyvinylidene fluoride (PVDF) and polyvinylidene chloride (PVDC) are compared in Figure 12. These materials were obtained as sieve fabrics for filter applications. A weak signal at around 3,000 cm⁻¹ is observed and relates to C-H stretching vibrations. For PVDF, a strong signal at 1,163 cm⁻¹ is observed, which can be attributed to the C-F stretching vibration [82]. For PVDC, a signal at 656 cm⁻¹ can be attributed to the C-Cl stretching vibration [83]. In this spectral range, however, other deformation vibrations related to the -CH₂- unit can also appear, making it difficult to accurately attribute the signal [13]. The medium signal at 1,743 cm⁻¹ could be caused by the stretching vibration of a C=O bond [13]. Due to the chemical structure of PVDC, there should be no C=O group with a related IR signal. However, chlorinated polymers such as PVDC or PVC are sensitive to photooxidation. For this reason, the appearance of C=O carbonyl groups can be the result of such photooxidative processes [83].



Figure 12: IR-spectra of the materials polyvinylidenfluoride (PVDF) and polyvinylidenchloride (PVDC) in comparison. Both materials were obtained as sieve fabrics for filter applications.

4.7 Polyphenylene sulfide (PPS)

The high-performance properties of polyphenylene sulfide (PPS) fibres can be summarized by two statements: a high chemical stability, which is nearly as good as PTFE fibres, while the chemical stability of PPS fibres against high concentrated acids and alkali is extremely high, even near the boiling point of these liquids. Moreover, most organic solvents cannot damage PPS fibres [21, 23]. PPS fibres are only sensitive to oxidative agents such as hydrogen peroxide (H_2O_2) or nitric acid (HNO₃). Also, oxygen from the atmosphere can damage PPS fibres at elevated temperatures. These oxidative agents attack the PPS polymer at the sulphur bridge -S- through the oxidation of the -SO- and -SO₂- units. Filter materials made from PPS are used for the filtration of hot gases and aggressive media. PPS fibre materials are also used as sewing yarns for application with aggressive chemicals. The chemical structure of PPS is quite simple. PPS is the sulphur-containing, high-performance fibre with the greatest commercial relevance. Its chemical structure is depicted in Scheme 10. Other sulphur-containing, high-performance fibres are based on the polymer polysulfonamide (PSA), and are supplied under the tradename Tanlon. PSA fibres are especially known for their fire-retardant properties [84, 85].

An IR-spectrum taken from a filter material made from PPS non-woven material is shown in Figure 13. The weak signal at 3,065 cm⁻¹ can be attributed to C-H stretching vibrations of hydrogen atoms placed at the aromatic ring. The signals at 1,490 cm⁻¹ and 1,568 cm⁻¹ can be attributed to C=C vibrations from the benzene ring [86]. The signal at 804 cm⁻¹ can be attributed to the C-H deformation vibration, which is typical for a 1.4 substitution of an aromatic ring system with two neighbouring hydrogen atoms [13].



Scheme 10: Chemical structure of polyphenylene sulfide (PPS)



Figure 13: IR-spectrum of polyphenylene sulfide (PPS)

4.8 Polyphenylene-benzobisoxazol (PBO)

Fibres made from polyphenylene-benzobisoxazol (PBO) combine several advantageous properties. The chemical structure of PBO fibres is depicted in Scheme 11. They are built up using an heteroaromatic rigid rod polymer chain. PBO fibres have the highest maximum temperature of usage of all commercially available synthetic fibres. The LOI value of PBO fibres is reported to be in the range of 56 to 68 [21, 23]. This high LOI value is especially remarkable because PBO does not contain any kind of halogen atom in its chemical structure. The mechanical strength of PBO fibres is high, so it is also used for the production of high-strength ropes. PBO fibres are also distributed under the tradename Zylon fibres.

Figure 14 shows the IR-spectrum of a PBO (Zylon) sample that was taken from a two-component rope. The core of the rope is braided from HPPE fibres, while the surface layer is braided from PBO fibres. The weak signal at 3,092 cm⁻¹ can be attributed to C-H stretching vibrations from H-atoms bonded to an aromatic ring system. The signal at 1,620 cm⁻¹ can be attributed to the C=N stretching vibration, which is part of the heteroaromatic system, while the signal at 1,053 cm⁻¹ can be attributed to the C-O stretching vibration of the -C-O-C- unit, which is also part of the heteroaromatic system [87]. The three signals at 1,412 cm⁻¹, 1,495 cm⁻¹ and 1,568 cm⁻¹ can be

attributed to C=C vibrations from the aromatic ring systems. The signal at 844 cm⁻¹ can be attributed to the C-H deformation vibration, which is typical for a 1.4 substitution of an aromatic benzene with two neighbouring hydrogen atoms [13].



Scheme 11: Chemical structure of Polyphenylene-Benzobisoxazol (PBO), supplied as PBO fibres also under the tradename Zylon



Figure 14: IR-spectrum of polyphenylene-benzobisoxazol fibres (PBO) taken from a braided fibre sample

4.9 Resin-based fibres

Fibres can be also produced from resins. In the category of resin-based fibres, primarily two different types of resin-based fibre should be mentioned: melamine and phenol-based resins. Melamine fibres were previously distributed under the tradename Basofil. They are actually distributed as smart melamine fibres [88, 89]. Fibres from phenol resins are also referred to as novolac fibres and distributed under the tradename Kynol fibres [90]. These fibres exhibit flame-retardant properties, are selfextinguishing in contact with fire and exhibit low smoke formation. Nonwoven materials made from Kynol fibres can also be used as heat insulation material [91]. The chemical structure of resin-based fibres made from Kynol is given in Scheme 12. Resin-based fibres are built up using an irregularly crosslinked three-dimensional network. Textile materials made from Kynol fibres exhibit a typical orange coloration, which can be modified by laser treatment [92]. The related IR-spectrum of a novolac fibre is present-

ed in Figure 15. The broad signal at a maximum of

3,377 cm⁻¹ can be attributed to the O-H stretching vibration of the hydroxy groups. The weak signals between 2,849 to 3,009 cm⁻¹ can be attributed to various C-H stretching vibrations. The signal at 3,009 cm⁻¹ can probably be attributed to C-H units that are part of the aromatic benzene rings. Both signals at 2,916 cm⁻¹ and 2,849 cm⁻¹ can be attributed to C-H stretching vibrations from the aliphatic -CH₂- unit [13]. The strongest signal at 1,219 cm⁻¹ probably relates to the stretching vibration of C-O bonds. The signals at 1,601 cm⁻¹ and the double signal at 1,470 cm⁻¹ can be attributed to C=C stretching vibrations in the aromatic ring [13]. However, the signal at 1,470 cm⁻¹ can be also attributed to the deformation vibration of the -CH₂- unit.



Scheme 12: Chemical structure of a resin-based fibres – novolac resin



Figure 15: IR-spectrum of fibres made from novolac resin (Kynol fibres)

5 Inorganic fibres

Inorganic materials are materials that are not built up using carbon-hydrogen compounds. In accordance with this definition, inorganic fibres are all fibres that are not built up by the chemical elements carbon and hydrogen. The main categories of inorganic fibres are glass fibres, ceramic fibres, metal fibres and carbon fibres [93]. In comparison to organic synthetic fibres, inorganic fibres contain a high thermal stability up to several hundred °C and even in excess of 1,000 °C even in presence of oxygen. Inorganic fibres from metal oxides are also not flammable and are thus used to produce fibres for high-temperature and flame-resistant applications.

The IR-spectra of some inorganic fibres built up using mixtures of different metal oxides are presented in Figure 16. These fibres were selected for this review because of their technical relevance and the fact that other inorganic fibres, such as metal fibres, SiC fibres and carbon fibres, do not exhibit significant signals in the studied spectral range of infrared light.



Figure 16: Comparison of the IR-spectra of different inorganic fibres

E-glass fibres are probably the most used glass fibre type and are mainly built up using silica (SiO_2) and alumina Al_2O_3 [94]. For E-glass fibres, the dominant signal in the infrared spectrum occurs at around 1,000 cm⁻¹ and can be attributed to the vibration of the group -Si-O-Si [95]. The second signal at around 800 cm⁻¹ can be also attributed to a -Si-O- vibration [96].

The weak signal at around 1,390 cm⁻¹ has been attributed by some authors to the absorption of other oxides such aluminium oxide or boron oxide [97]. However, this signal more likely relates to the presence of organic sizing agents on fibre surfaces. The surface of glass fibres is usually treated with small amounts of organic compounds to protect the glass fibres and to improve their mechanical properties. This mechanical protection is especially necessary during yarn and fabric production processes. Caramelized E-glass fibres are thermally treated under moderate conditions, so the organic compounds on the glass fibre surface are partly decomposed. For this reason, a typical brown (caramelized) coloration of the glass fibre appears. The IR-spectra of E-glass fibres and caramelized E-glass fibres are nearly the same. Beside caramelization, E-glass fibres can be also modified using natural inorganic compounds such as vermiculites. In this case, the IR-spectrum is determined by the composition of the inorganic vermiculite, which is placed on the surface of the E-glass fabrics. Vermiculite is a natural clay mineral that contains silicon and aluminium oxides, as well as magnesium oxides [98, 99]. The IR-spectra of E-glass fabric with vermiculite exhibit a broad signal with a maximum at 893 cm⁻¹ and a second broad signal at 675 cm⁻¹. In literature, this second maximum at 675 cm⁻¹ is attributed to the vibration of Mg-O or to the stretch vibration of the group Al-O-Si [98, 99]. In contrast to E-glass fibres, silica fibre fabric only contains SiO₂. The IR signal at 1,009 cm⁻¹ is more precise, while there is no signal around 1,390 cm⁻¹. Basalt fibres are produced by melting natural volcanic rocks (basalt stones). Beside silica and alumina, basalt fibres also contain significant amounts of other metal oxides, e.g. from iron or titanium [94, 100–103]. Basalt fibres can be also used as a coating additive to introduce UV-protective properties [103]. Due to the presence of iron oxide, basalt fibres exhibit a typical brown coloration. The IR-spectra of the basalt fibre presented in Figure 16 was recorded from a commercially available monofilament. This IRspectrum shows one broad signal with a maximum at 883 cm⁻¹. In comparison with the IR-spectra of basalt fibres reported in literature, this maximum appears at a lower wavenumber than in articles reporting a maximum of between 1,000 cm⁻¹ and 1,100 cm⁻¹ for basalt fibres [100, 104]. However, it should be clear that the IR-spectrum of a commercial basalt fibre product is influenced by the broad range of possible basalt composition and by the possible treatment of the fibre surface [100, 104].

6 Conclusions and future perspectives

In addition to conventional fibres (such as polyester (PET), polyamide (Nylon), cotton, etc.), there are many different high-performance fibres on the market that exhibit outstanding properties, giving them an advantage over conventional fibres. Of course, it is not possible in the scope of this review to present information regarding each fibre type. For this reason, the focus was mainly on high-performance fibres with a significant commercial importance. The production rate of high-performance fibres is quite low compared to conventional fibres. Nevertheless, several high-performance fibres are of significant economic relevance, and are essential for many products and technical processes.

There is one main question for the future perspectives of high-performance fibres: Can new high-performance fibres establish a foothold on the market in the future? Actual trend materials is this respect are most likely fibres made from carbon nanotubes (CNTs) or graphene compounds [105-107]. Also, fibres developed using a bionic approach, such as spider silk, could gain in importance in the future. Another possible future trend could also be the reinvention and commercialization of fibre types developed in the past. Current examples of this trend are found for regenerated protein fibres or melamine-based resin fibres. Another possible candidate for reinvention could be fibres made from inorganic polymers, especially polyphosphazenes. A higher elasticity than elastane fibres has been reported for these fibres. Due to the high content of phosphorous and nitrogen, these fibres also exhibit flame-retardant properties. Such a combination of properties has made them highly interesting, especially as additive fibres in fire-protective garments [73, 108].

It should be clear, that market demand for high-performance fibres will continue to be high in the future, and there will, of course, be new material developments leading to advantageous materials with surprising properties.

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