Electrospun Nanofibre Mats Coating - New Route to Flame Retardancy

Emanuela Gallo, Ziyin Fan, Bernhard Schartel, Andreas Greiner

► To cite this version:

Emanuela Gallo, Ziyin Fan, Bernhard Schartel, Andreas Greiner. Electrospun Nanofibre Mats Coating - New Route to Flame Retardancy. *Polymers for Advanced Technologies*, 2011, 22 (7), pp.1205. 10.1002/pat.1994 . hal-00647885

HAL Id: hal-00647885

<https://hal.science/hal-00647885>

Submitted on 3 Dec 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Electrospun Nanofibre Mats Coating - New Route to Flame Retardancy

Journal:	<i>Polymers for Advanced Technologies</i>
Manuscript ID:	PAT-11-009.R1
Wiley - Manuscript type:	Short Communication
Keywords:	electrospinning, polyimide, nanofibres, fire retardancy

SCHOLARONE™
Manuscripts

Review

Short Communication:

Electrospun Nanofibre Mats Coating - New Route to Flame Retardancy

E. Gallo,^a Z. Fan,^b B. Schartel,^{a*} A. Greiner^b

^a BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany

^b Philipps-University Marburg, Department of Chemistry and Scientific Center for Materials Science, Hans-Meerwein-Straße, 35032 Marburg, Germany

Abstract

A novel route towards halogen-free fire retardancy of polymers through innovative surface coating is described. Nanofibre mats based on polyimide are deposited on PA66 through electrospinning. Scanning electron microscopy (SEM) is used to characterize the nanofibres. Cone calorimeter tests were performed to evaluate the fire performance. Due to their low thermal conductivity, electrospun nanofibre mats act not only as sacrificial layers, but also as a protective surface that delays ignition. The effect is influenced by the fibre diameters and the imidization.

Keywords: electrospinning; polyimide; nanofibres; fire retardancy

*Correspondence to: Tel.: +49 30 8104 1021; Fax: 49-30-8104-1617

E-mail: bernhard.schartel@bam.de (B. Schartel)

Introduction

Since the major trend in the fire retardancy of polymers is to reduce and replace problematic compounds with ecologically friendly additives, fire protection coatings are considered to be a promising and innovative route. Unlike other classical approaches, surface modification processes^[1,2] do not involve high loadings of additive fire retardants, since the flame retardancy is concentrated exclusively within the surface layer. Furthermore, by using fire protective coating, additives are not incorporated within the material, preventing deterioration of its intrinsic properties (e.g. the mechanical properties) and maintaining easy processibility.

Fire protection coatings, acting through the phenomena of intumescence,^[3] form an expanded multicellular layer when heated, which protects the underlying material from the action of the heat flux or flame. As a consequence, intumescent coatings must be optimized to work in time to have a fire retardant effect, as they intrinsically belong to a later stage, because it takes time for the protective intumescent layers to form. Thus in contrast to intumescent coatings, a fire protective layer placed at the key position in the material – the interface between the condensed and gas phase – can be effective from the beginning, even in the first stages of decomposition. A “sacrificial” layer can protect a flammable substrate, in particular by delaying its ignition. Nevertheless, once the layer is consumed, the burning of the substrate may no longer be retarded. This means that the sacrificial layers must be efficient or thick enough to provide fire protection. However, a clear increase in time to ignition can be an excellent overall approach for flame retardancy.^[4]

Covering one polymer by another more temperature-resistant or fire-resistant polymer is indeed a reasonable approach to reducing flammability without using additive flame retardants. Polyimides (PI) are an important group of high-performance polymers, popular in many technological applications due to their excellent thermal behaviour, very good chemical resistance and electrical properties.^[5] Because of these outstanding properties, PI has found extensive application as fibres, films, coatings and composites. However, many aromatic PI are neither soluble nor fusible because of the high rigidity and conjugation of their backbone. These drawbacks cause difficulties in fabrication and limit their applications.

Ultra-thin polyimide nanofibres are made by means of electrospinning.^[6-9] The process involves the application of a strong electrostatic field to a stream of polymer precursor solutions and subsequent imidization.^[10] The electrostatic field creates instabilities in the polymer stream, thereby producing ultrafine fibres, often in the nanoscale range. The low density of collected nanofibre mats, similar to that of foam, can provide an additional good thermal insulation for the underlying material.

In this work, a new route for flame retardancy by protective coating has been explored. By electrospinning and electrospinning followed by thermal treatment, thin films of poly(amic acid) (PAA)-nanofibre mats and PI-nanofibre mats, respectively, are laid down on PA66 substrates. The fire behaviour and thus the flame retardancy properties are evaluated using the cone calorimeter. PAA-nanofibre mat and PI-nanofibre mat coated PA66 are compared to PAA-film and PI-film coated PA66, respectively. Additionally, free standing PI nanofibre fabrics are investigated to get an insight into the fire behaviour of the nanofibre mats themselves. The impact of nanofibre thickness as well as imidization of PAA to PI is discussed.

Experimental Part

Materials

PA66 (Ultradid, BASF AG, Germany) was used as substrate in the form of plates (100 x 100 x 3 mm). 4,4-oxydianiline (ODA) 98% and pyromellitic dianhydride (PMDA) 97% were purchased from Alfa Aesar. ODA was recrystallized from toluene and PDMA was sublimated at 250°C before use. N,N-dimethylformamide (DMF) was dried using a molecular sieve and distilled before use.

Synthesis of PI and its precursor

The PI synthesis was conducted in two steps (Fig. 1): the synthesis of the PAA precursor and the subsequent imidization process of PAA to PI. During the first step the precursor PAA was synthesized through a polyaddition between equimolar amounts of dianhydride (PMDA) and diamine (ODA). A 3-necked 250 ml flask equipped with a mechanical stirrer, argon inlet and outlet was charged with 0.04 mol of ODA and 70.5 ml of DMF. The mixture was stirred under flow of dry argon until the complete dissolution of solids, and then cooled below 10°C using an ice bath. An equimolar amount of PMDA (0.04 mol) was added to the reaction solution in portions. The precursor solution was stirred vigorously at room temperature for 24 h before being diluted into three different concentrations from 20 to 15 wt%. Three solutions were prepared, PAA-20, PAA-18 and PAA-15, whereby the last part of the name indicates the corresponding concentration in wt%. Two additional materials were produced, PAA-film and PI-film coated PA66 substrates. In both cases the polymer solution was not electrospun, but a thin film of PAA precursor solution was deposited on the PA66 matrix by solvent evaporation. The transparent coatings were around 80 µm and 108 µm thick. Corresponding free-standing nanofibre PI fabrics (100 mm x 100 mm, 0.5 g) were also investigated for comparison.

Preparation of electrospun nanofibres and imidization

The electrospinning process was performed using electric fields of the order of 100 kV m^{-1} , from a 15 kV electrical potential applied to a 12 cm gap between the spinneret and a rotating disc collector. All the PAA precursor solutions were processed by electrospinning on rotating PA66 plates. To ensure adhesion between the PA66 substrate and the nanofibres, DMF was spread on the PA66 plates allowing the first electrospun fibres to stick on the surface. The imidization process (referred as second synthesis step) was accomplished by exposing solution-cast or electrospun nanofibre mat coated PA66 plates in a high-temperature furnace, preceded by vacuum-drying the PAA precursors in order to remove any residual solvent. In order to find the ideal imidization conditions, FTIR spectroscopy was used to follow the imidization reaction. During the imidization the intensity of CH-vibration did not change, while the intensity of CO-vibration increased with the degree of imidization. By comparing the relative intensity changes of the characteristic peaks of the CH-bonds and the C=O-bonds, the degree of the imidization was measured. The best conditions were found to be the treatment of the precursor at 453 K for 24 h. The second step related to the imidization reaction is shown schematically in Fig.1.

Characterization

Cone calorimeter (Fire Testing Technology, FTT, UK) according to ISO 5660 was used to characterize the fire behaviour. PA66, PAA-nanofibre mat coated PA66 (PAA-20, PAA-18, and PAA-15), PI-nanofibre mat coated PA66 (PI-20, PI-18, and PI-15), PAA-film coated PA66 (PA-film) and PI-film coated PA66 (PI-film) were investigated. Additionally, free standing PI nanofibre fabrics are investigated to get an insight into the fire behaviour of the nanofibre mats. Samples of 100 mm x 100 mm x 3 mm were first conditioned at 23°C and 50 % r.h. to equilibrium and then irradiated horizontally at a heat flux of 50 kW m^{-2} . Specimens were placed in an aluminium tray. The surface of the specimen was exposed to the irradiation at the distance of 25 mm from cone heater. The aluminium trays were placed on refractory fibre blanket on top of a ceramic board. The free-standing PI nanofibre fabrics were additionally placed in a metal wire cage. The wire cage was formed from a 220 mm x 100 mm sheet of steel mesh (1 mm wire with 10 mm mesh size) around a solid template 3 mm x 100 mm x 100 mm. Most of the samples were measured in triplicate, some of the coated only in duplicate due to a lack of specimen. The latter is strictly speaking not according to ISO 5660, but however the reproducibility was convincing in all cases. The results were averaged. Scanning electron microscopy (SEM) was used to analyze the dispersion and the size of the nanofibres prepared from different solutions.

Results and Discussion

Morphology and Diameter

The morphology and diameter of electrospun fibres are dependent on the processing parameters^[11] and were investigated by SEM. The images of electrospun nanofibres before and after imidization are illustrated in Fig. 2. The nanofibres were randomly distributed to form a three-dimensional fibrous network. Different fibre diameters were observed. The results are summarized in Table 1. The average diameter of the nanofibres is affected by the concentration of the precursor solution: the higher the solution concentration, the thicker the corresponding diameter of the nanofibres. The presence of beads in PAA-15 electrospun fibres is a common phenomenon when low viscosity solutions (low concentration) of polymer are used. The density of beads was dramatically reduced as the concentration of the solution increased.

Fire Behaviour: Visual Observations

The visual observation of free-standing PI nanofibres fabrics without any substrate in the cone calorimeter gave a hint of the fire behaviour by PI nanofibre mats used for coating PA66. Neither real ignition nor real flaming combustion were observed, but rather a thermo-oxidative decomposition process. The surface of the nanofibre fabrics exhibited only small surface flames and glowing until the nanofibres were completely consumed and no residue remained. It is concluded that the low density and the large surface-area-to-volume ratio causes this fire behaviour characteristics.

PA66 specimen showed the formation of a dark solid skin before ignition. This skin formation was described before for PA66 and ascribed to the thermo-oxidative decomposition of the PA66 surface.^[12] The subsequent deformation due to large bubbles under this skin was interpreted as anaerobic decomposition since the skin did not increase in thickness. The bubbling resulted in an unsteady gas release and therefore in some uncertainty in the time to ignition. After ignition, even in the well-ventilated conditions of the cone calorimeter, pyrolysis of the condensed phase is essentially anaerobic. The oxidation taking place in the gas phase (flame zone) consumed all oxygen above the specimen surface. All of the investigated materials burned homogeneously and completely with a stable flame zone above a bubbling liquid surface. The intense boiling and bubbling noted during flaming combustion left behind hardly any char.

In the film-coated samples, before ignition, the superficial layer first turned a darker colour and then started melting. Once ignition occurred, a boiling and bubbling liquid consisting

of decomposing PA66 and the original film was observed during flaming combustion. The polymer was completely consumed and no residue was left at the end of burning.

The surface behaviour of the electrospun fibre mats coated PA66 (PAA-20, PAA-18, PAA-15 and PI-20, PI-18, PI-15) was affected by the different surface behaviour. In contrast to PA66, the superficial electrospun fibre mat layer covered the underlying material, preventing it from reaching the critical conditions of ignition for some time. This protection resulted in a significant increase in time to ignition. When the polymer underneath started decomposing, the produced fuel accumulated under the skin as long as the surface layer was undamaged (Fig. 3a). When the surface layer cracked, ignition occurred and a kind of flashing was observed (Fig. 3b). After ignition the polymeric material burned homogeneously with a stable flame (Fig. 3c). Hardly any char remained after combustion (Fig. 3d). No significant change in the residue formation was detected among the materials.

Fire Behaviour: Ignitability

The influence on ignitability using the time to ignition (t_{ig}) was monitored (Table 2). The ignition time reported in Table 2 for free-standing nanofibre fabrics (184 s) indicates when the glowing began. All of the coated PA66 showed t_{ig} increased compared to PA66. The influence of three parameters was discussed: 1) nanofibre mats instead of films, 2) imidization comparing PAA-film and PI-film coated PA66 as well as PAA and PI nanofibre mat coated PA66 specimen and 3) fibre thickness of the electrospun PAA and PI fibre mat coatings.

The different behaviour of nanofibre mat and film coatings on the t_{ig} is presented in Fig. 4 (heat release rate, HRR, versus time). No improvement on t_{ig} was achieved for PAA-film coated PA66 in comparison to PA66. For both series, PAA (4a) and PI (4b), nanofibre mat coatings performed better than the corresponding film coating: PAA-film ignites after 39 s, while through the PAA fibre mat series the t_{ig} is shifted up to 72 s. In the case of PI coated PA66 samples, PI-film increased the t_{ig} up to 60 s in comparison to PA66, but again, this effect was bigger for the corresponding samples with PI nanofibre mat coating (Fig. 4b). In conclusion, specimens coated with electrospun nanofibre mats perform better than the corresponding film samples with respect to improving the t_{ig} . Using nanofibre mats, the original function of the surface layer was switched from a “sacrificial” one to a protective one thanks to an additional thermal insulation effect.

The effect of the imidization process on the t_{ig} for the three concentrations investigated is reported in Table 2. Through imidization, the less stable PAA precursor was converted into the more thermal stable PI. The formation of a more thermally stable barrier resulted in better protection of the underlying PA66 material and in a further shift in the t_{ig} . The influence of fibre

diameter on shifting the t_{ig} for PAA and PI series is presented in Fig 4. In comparison to PA66, the biggest improvement in time to ignition was achieved with PAA-20 and PI-20. The thicker the fibres, the bigger the shift in t_{ig} to later times.

Fire Behaviour: Heat Release and Smoke

The maximum HRR (PHRR) and the total heat evolved (THE) are two other important fire behaviour characteristics determining the fire risks. The effective heat of combustion (EHC = THE/TML, with TML = total mass loss) is a suitable measure for the gas-phase activity. As the main fire hazard, the production of smoke and CO was also considered. Table 2 summarizes all of the evaluated cone calorimeter results. Fig. 5 displays the HRR curves of nanofibre fabrics without substrate (a) and the two different series of investigated nanofibre mat coated materials, PAA and PI (b,c,d). The shape of the HRR curve gave some insight into the fire behaviour of the different materials. The HRR of the nanofibre fabrics started decomposing without a real flaming process and reached an extremely small PHRR of only 18 kWm^{-2} at 200 s. Due to the small quantities measured in the cone calorimeter test for this material, only the t_{ig} , PHRR and THE were evaluated and the corresponding uncertainties are reported separately in Table 2. PA66 showed a HRR curve with a maximum corresponding to the PHRR and a shoulder occurring immediately after ignition. The shape of the curve remained substantially unchanged for the coated materials. The differences in the heat and smoke release among the materials were discussed in terms of different parameters.

Neither PAA-film coated nor PI-film coated PA66 significantly altered the PHRR in comparison to PA66 (Fig. 4a, b). Comparing PAA-film coating with the corresponding nanofibre mat coatings (Fig. 4a) the peak increased slightly in PAA-18 and PAA-20, while no difference was detected for PAA-15. No important change was observed between the PHRR of PI-film and PI-nanofibre mat coated series (Fig. 4b). The THE seemed to be slightly higher in the film-coated samples than the corresponding nanofibre mat-coated ones. EHC, which is normally decreased by gas-phase mechanisms, was slightly reduced by film coating in comparison to fibre mats. As regards uncertainty, the amount of smoke release is unchanged between nanofibres and the film samples.

The PHRR of PA66 was not reduced by imidization of PAA-coatings to PI-coatings, as depicted for the three sets of materials in Fig. 5 (b,c,d). PHRR of PI samples was always higher than for the corresponding PAA samples. The higher thermal resistance of the PI-nanofibre mat, in comparison to the corresponding PAA-nanofibre one, delayed the ignition time. Before ignition, the material underneath is preheated and begins decomposing. Fuel accumulates under the surface layer. A prolonged time to ignition implies that the preheated material and gaseous

decomposition products have more time to accumulate under the protective layer. This accumulation resulted in an increased reaction when the superficial layer broke and ignition occurred. This effect is proposed to be responsible also for the higher PHRR in comparison to PAA samples. On the contrary, early ignition of PA66 resulted in a lower accumulation of combustible vapours to yield a lower PHRR after ignition. The near-constant THE and EHC suggested an unchanged decomposition mechanism with respect to the effective heat of combustion of the volatiles. No particular effect was detected on the smoke production parameters.

The fibre diameter had an influence on the PHRR (Fig. 4). In comparison to PA66, the PHRR was clearly increased in the PAA series with increasing fibre diameter (up to 20% in PAA-20). In the PI series this trend was no longer so clear, as PI-15 has a higher PHRR than PI-18 and PI-20. The diameter of the fibres did not affect other parameters like fire load (THE), EHC and smoke; however, minor effects on the order of $\pm 10\%$ variation were observed.

Fire Behaviour: Flame Spread Indices

Fire growth rate (FIGRA), maximum average rate of heat emission (MAHRE) and $\text{PHRR}/t_{\text{ig}}$ are three fire safety engineering indices introduced as measures to assess the main hazards of developing fires. FIGRA is the largest slope in the HRR *versus* time, which is believed to represent the propensity of the material for fire growth. The MAHRE index was used to assess materials, taking into account the HRR and the total heat release (THR) over time. $\text{PHRR}/t_{\text{ig}}$ was proposed empirically since PHRR and t_{ig} may well account for the two characteristics controlling flame spread: HRR of the burning area and ease of ignition of the surrounding area. All three of these indices concentrate relevant information into a single number, which is clearly an oversimplification.^[13] The calculated values for FIGRA (in this case estimated as $\text{PHRR}/\text{time to peak}$), MAHRE and $\text{PHRR}/t_{\text{ig}}$ are presented in Table 2 and provide a qualitative ranking of the fire hazard of the materials. In comparison to PA66, in all of the coated materials a general reduction in the propensity for fire growth and flame spread was observed.

Compared to PA66, for the PAA-film-coated PA66, FIGRA and $\text{PHRR}/t_{\text{ig}}$ remained unchanged; only MAHRE showed a reduction of 20%. For the PI-film, a slight reduction in FIGRA occurred (12%), whereas MAHRE was decreased by 30% and $\text{PHRR}/t_{\text{ig}}$ by 35%. The reduction in MAHRE was larger for the films than for the nanofibre mats due to the increased PHRR increasing the AHRE. In contrast FIGRA and $\text{PHRR}/t_{\text{ig}}$ took advantage of the delayed t_{ig} and heat release, respectively. A further decrease was observed when the nanofibre mat layer was used instead of the film for both PAA-nanofibre and PI-nanofibre coated samples. The reduction observed for PAA nanofibre mat coatings was up to 28% in FIGRA, and 45% in

PHRR/ t_{ig} . The reduction observed for PI nanofibre mat coatings was up to 18% in FIGRA, and 50% in PHRR/ t_{ig} . Compared to PA66, the PI-film coating reduced all indices clearly more than the PAA-film, again indicating the benefit of imidization. In contrast, comparing PAA and PI-nanofibre mat coated samples reveals a rather muddled role of imidization, in the same order of magnitude as the uncertainty. Whereas using nanofibre mat coatings has a clear flame retardancy effect compared to PA66 with respect to all indices, the fibre diameter hardly had a significant effect in the flame spread indices. Some tendency toward decreasing flame retardancy occurred for PAA-nanofibre, and toward an increasing one for PI-nanofibre mats with increasing fibre thickness.

Conclusions

PAA based on reacting PMDA and ODA were successfully electrospun using concentrations in the range from 15 to 20 wt% on PA66 substrates forming a thin superficial nanofibre mat layers. By thermal treatment they were transformed into PI nanofibre mat coatings. The fire behaviour was investigated by means of cone calorimeter and compared to free-standing PI nanofabrics, PA66 and PA66 coated with PAA and PI films, respectively. The formation of a thin protective layer consisting of nanofibre mat has its main effect in delaying the t_{ig} . The data deliver no hint of a change in the chemical processes in the gas and condensed phase reducing the fire hazard of the underlying PA66. The nanofibre mat coatings are concluded to work via physical effects changing the mass or heat transport between the pyrolysis and the flame zone. In comparison to the corresponding film coated PA66 it became clear that the PAA and the PI nanofibre mat coatings are not only sacrificial, but also protective layers due to advanced thermal insulation. Different parameters affect the delay in ignition. Imidization of PAA to PI increases the thermal stability of the coatings, resulting in an enhanced delay in t_{ig} . Increasing the PAA precursor concentration increased the fibre diameter within the electrospun PAA and PI nanofibre mats and resulted in a further increase.

Of course the achieved delay in ignition in the investigated systems is probably not large enough to offer sufficient flame retardancy with respect to commercial exploitation. Increasing the shift in t_{ig} , additional reduction in PHRR or the combination with established flame retardants are obvious next steps of development when following this new approach presented here the first time. In this regard, it should be noted that the low density and large surface-area-to-volume ratio of PI nanofibre fabrics and PI nanofibre mat coatings, respectively, result in smouldering-like fire behaviour. On one hand this fire behaviour is an advantage with respect to fire risks such as HRR. On the other hand it is accompanied by a thermo-oxidative pyrolysis of the PAA and PI nanofibre mats without forming any residual protective layer. In contrast to what

was expected from the charring fire behaviour of PI, the PI nanofibre mats did not show any potential to decrease the PHRR of PA66 pyrolysis to a later stage.

However, the increase in t_{ig} and the discussion on different indices believed to indicate flame spread and fire growth rate, respectively, underline the potential of the concept already. The use of electrospun nanofibre mat coatings is proposed as a promising new route to improve the fire retardancy of polymers.

References

- [1] S. Bourbigot, C. Jama, M. Le Bras, R. Delobel, *Polym. Degr. Stab.* 1999 ; 66 , 153.
- [2] B. Scharrel, G. Kuhn, R. Mix, J. Friedrich, *Macromol. Mater. Eng.* 2002 ; 287 , 579.
- [3] H.L. Vandersall, *J. Fire Flammability* 1971 ; 2 , 97.
- [4] E. Wenz, T. Eckel, B. Scharrel, U. Beck, A. Hertwig, M. Weise, J. Strümpfel, E. Reinhold, Patent n. WO/2006/131229.
- [5] P.M. Hergenrother, *High Perform. Polym.* 2003 ; 15 , 3.
- [6] D.H. Reneker, I. Chun, *Nanotechnology* 1996 ; 7 , 216.
- [7] C. Nah, S.H. Han, M.H. Lee, J.S. Kim, D.S. Lee, *Polym. Int.* 2003 ; 52 , 429.
- [8] A. Greiner, J.H. Wendorff, *Angew. Chem. Int. Ed.* 2007 ; 46 , 5670.
- [9] R. Dersch, M. Graeser, A. Greiner, J.H. Wendorff, *Aust. J. Chem.* 2007 ; 60 , 719.
- [10] D.H. Reneker, A.L. Yarin, H. Fong, S. Koombhongse, *J. Appl. Phys.* 2000 ; 87 , 4531.
- [11] A. Frenot, I.S. Chronakis, *Curr. Opin. Colloid. Interface Sci.* 2003 ; 8 , 64.
- [12] B. Scharrel, R. Kunze, D. Neubert, *J. Appl. Polym. Sci.* 2002 ; 83 , 2060.
- [13] B. Scharrel, T.R. Hull, *Fire Mater.* 2007 ; 31 , 327.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Tables

Table 1 Diameter of fibres for the investigated samples

Sample	Fibre diameter (nm)
PAA-20	395 ± 92
PAA-18	312 ± 94
PAA-15	107 ± 32
PI-20	378 ± 98
PI-18	308 ± 82
PI-15	109 ± 32

Table 2 Cone calorimeter results (irradiance 50 kWm⁻²)

	t_{ig}	PHRR	THE	EHC	TSR	CO	FIGRA	MAHRE	PHRR/t_{ig}
	s	kWm ⁻²	MJm ⁻²	MJm ⁻² g ⁻¹	m ² m ⁻²	kg/kg	kW/m ² s	kWm ²	kWm ⁻² s ⁻¹
<i>Error</i>	± 2	± 50	± 2	± 0.02	± 250	±0.002	± 0.8	± 25	± 0.8
PI nanofibre fabrics	184	18± 5	1± 0.5	-	-	-	-	-	-
PA66	38	1230	97	2.87	811	0.021	9.3	520	32.4
PAA-film	39	1257	105	2.52	805	0.011	9.5	412	32.2
PAA-15	61	1086	95	2.80	756	0.018	6.7	420	17.8
PAA-18	70	1327	98	2.88	669	0.017	7.8	475	18.9
PAA-20	72	1481	99	2.91	673	0.020	7.7	448	20.6
PI-film	60	1276	105	2.80	776	0.014	8.2	382	21.3
PI-15	75	1447	103	3.06	663	0.019	7.9	492	19.3
PI-18	71	1322	98	2.92	693	0.019	8.6	468	18.6
PI-20	85	1363	99	2.92	810	0.019	7.6	452	16.0

Figure captions

Figure 1. Schematic diagram of condensation between dianhydride PMDA and diamine ODA to form the corresponding polyamic acid (PAA), as well as the imidization of PAA into a polyimide (PI).

Figure 2. SEM pictures (from left to right) of: PAA-20, PAA-18, PAA-15 (first row) and PI-20, PI-18, PI-15 (second row).

Figure 3. Burning behaviour during cone calorimeter experiment for modified PA66 samples.

Figure 4. Cone calorimeter results: comparison between film and nanofibres for PA66 and a) PAA-film and PAA-15, PAA-18, PAA-20 and b) PI-film and PI-15, PI-18 and PI-20.

Figure 5. Cone calorimeter: heat release rate curve for a) nanofibres; PA66 and b) PAA-15 and PI-15; c) PAA-18 and PI-18; d) PAA-20 and PI-20.

45x11mm (600 x 600 DPI)

533x289mm (300 x 300 DPI)

Peer Review

32x6mm (600 x 600 DPI)

For Peer Review

177x124mm (600 x 600 DPI)

177x125mm (600 x 600 DPI)