# EFFECT OF MONTMORILLONITE CONTENT AND THE TYPE OF ITS MODIFIER ON THE THERMAL PROPERTIES AND FLAMMABILITY OF POLYIMIDEAMIDE NANOCOMPOSITE FIBERS

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The effects of montmorillonite (MMT) content (1, 3, 5%) and the type of its modifiers on the thermal properties and flammability of PIA nanocomposite fibers have been assessed. Sodium montmorrilonite was modified with aminododecane acid and octadecylamine. Samples of PIA nanocomposite containing commercial MMT: Nanomer PGW from Nanocor were also included in the comparative analysis.

It has been found that the glass transition temperature ($T_g$) of the fibers under investigation depends on the type of MMT's modifier. On the other hand this parameter does not affect the thermal stability of fibers defined with $T_5$ and $T_{50}$ indicators since the thermal decomposition of modifiers takes place at lower temperatures.

The results of testing the flammability of PIA nanocomposite fibers containing 3% of variously modified MMT allow one to include them among flame-retardant fibers.

***Keywords:*** *fibre properties, flammability, nanocomposites, polyimidoamide, thermal stability*

## Introduction

The incorporation of nanoadditive in the form of MMT into polyimidoamide (PIA) polymer makes it possible to impart new features to the fibers and to improve their existing properties connected with the chemical structure of the fiber-forming polymer. The presence of aromatic rings and imide groups in the macromolecule provides good thermal properties of PIA fibers. Their high glass transition temperature at a level of 285°C makes it necessary to perform the second stage of thermal drawing at about 300°C under nitrogen in order to obtain a high tenacity over 35 cN/tex [1, 2]. Such an order of magnitude of this parameter however is not indispensable when PIA fibers are used for textile applications. It is rather desirable to have fibers with increased porosity and consequently with good sorption properties including especially a high value of water retention, which determine the comfort of using protective clothing as the so-called first-contact-with-flame clothes.

The modification of the fiber-forming polymer consisting in incorporating flexible segments derived from diaminodiphenylmethane resulted in the increased polymer susceptibility to deformation during the stage of plasticizing drawing. This made it possible to obtain fibers with tenacity of 15 cN/tex being suitable for textile processing [3–6]. At the same time, owing to a suitable selection of fiber-spinning parameters it was possible to increase the moisture absorption of fibers, maintaining their high thermal stability [7]. This however resulted in some decrease in the resistance to the action of thermal flux and flame. A considerable improvement in this effect was obtained by incorporating dispersed montmorillonite (MMT) into the modified PIA [8].

The tenacity of fibers from such a nanocomposite containing 3% of MMT (commercial Nanomer PGW from Nancor) is lower by 3%, which is connected with the presence of non-fiber-forming nanoadditive as well as the lack of complete exfoliation of MMT layers as confirmed by WAXS measurements [9]. At the same time, these fibers show increased porosity and moisture absorption as compared to those of the fibers from modified PIA without the nanoadditive.

The obtained sorption properties as well as the strength characteristics are affected also by the type of modifier used to change the MMT properties from hydrophilic to organophilic [10, 11]. The explanation of reasons for these differences, including the type of MMT dispersion (intercalation or exfoliation) in the fiber-forming polymer was made possible by the comparative analysis of the structures and properties of PIA

nanocomposite fibers containing various types of MMT. This was the subject of our previous paper [12]. The influence on the thermal properties and flammability of PIA fibers, besides MMT itself that is a natural clay characterized by a laminar interlayer cation structure (e.g. $Na^+$, $Ca^{2+}$) [13–17] can be also exerted by the quantity and type of the modifier used [18, 19].

The interactions between the modifier of MMT and the polymer macromolecules will be connected with the chemical structure of the modifier. The use of aminododecane acid as the modifier of MMT facilitates the formation of secondary bonds with amide groups of the polymer, which is rather impossible in the case of using octadecylamine as modifier. The chemical structure of modifier has also a bearing on the MMT dispersion in the polymeric matrix [9, 12]. We have found an extensive exfoliation of MMT packages in the PIA nanocomposite fibers containing MMT modified with aminododecane acid. On the other hand, in the fibers containing either MMT modified with octadecylamine or Nanomer PGW we have observed decreased inter-layer distances. These phenomena are requisites for the surface interaction between the polymeric matrix and MMT. This can also influence the thickness of MMT packages This may also influence the thickness of MMT packages; on their surfaces are formed layers of carbonised polymer during contact with flame. Thus, it creates a barrier that cuts off the oxygen access and heat energy limiting the oxidation of gaseous decomposition products. Such a barrier protection of the MMT dispersed in the polymer dominates over the increased air content in the system of pores of PIA nanocomposite fibers. This has been confirmed by us in our previous study concerning the comparison of thermal properties and flammability of PIA fibers containing with those of PIA fibers containing no nanoadditive [8].

The aim of the present study was to assess the effects of the type of MMT modifier and its content on the thermal properties and flammability of PIA nanocomposite fibers.

## Experimental

### Materials

The examined PIA fibers contained 1, 3 or 5% (in relation to polymer) of MMT modified either with aminododecane acid or octadecylamine and Nanomer PGW. All the fibres to be examined were spun at selected negative or positive value of as-spun draw ratio. This facilitated the preparation of PIA nanocomposite fibers with either increased strength or moisture absorption.

### Characteristics of spinning solution and montmorillonite

Fibers were spun from post-reaction solutions of PIA modified with diaminodiphenylmethane in N-methylpyrrolidone prepared in accordance with the conditions given in paper [6]. The solidification process was carried out in a bath containing an aqueous solution of the solvent (above 55%) at a low temperature, about 15–18°C. The drawing process was performed in a single stage, in a plasticising bath containing the same content of solvent as that in the coagulation bath, at an elevated temperature up to 65–70°C. Finally, solvent was rinsed off, and the resultant fibres were dried under isothermal conditions at 80–120°C. MMT in the form of a suspension in solvent in a quantity of 3% in relation to the polymer was added when the synthesis stage was completed. The analysis of the effect of MMT on the rheological properties of spinning solutions is given in [20].

Characteristic of MMT – Nanomer PGW is given in paper [21]. Characteristic of MMT modified with aminododecane acid is given in paper [10]. Characteristic of MMT modified with octadecylamine is given in paper [11].

### Fibre formation

Fibres were spun by the wet process from the PIA solution in N-methylpyrrolidone, using a spinning machine whose construction allowed one to stabilize the technological parameters at a required level under a continuous control. The spinnerets used had 240 orifices with a diameter of 0.08 mm.

### *Measuring and testing methods*

Fibre porosity was measured by means of a mercury porosimeter of Carlo-Erba linked with a computer system to register the numerical values of the measured parameters. The determination included: the total pore volume, total internal surface. This method allows one to determine the pore percentage content with given ranges in the capillary set with sizes of 5–7500 nm.

Moisture absorption at 65% and 100% RH was determined by the desiccator method according to the Polish Standard PN-81/P-04635.

Water retention was measured by the centrifuge method. Fibre samples were immersed in distilled water containing a surface-active agent (Rokafenol NX-3 in an amount of 0.1%) for 24 h and then the absorbed water was centrifuged off for 10 min at an acceleration of 10000 m s$^{-2}$.

Fibre tenacity and elongation at break were measured according to the European Standard

PN-EN-ISO-2062:1997, referring the breaking force to the fibre linear density in text.

The thermal analysis of fibres was carried out by means of a derivatograph, and thermogravimetry (TG), using a Paulik–Paulik–Erdey system derivatograph. The derivatographic analysis was carried out in air using weighed portions of 40 mg at a heating rate of 7.9°C min$^{-1}$ within the temperature range from 20 to 800°C.

## Results and discussion

As follows from the analysis of the data given in Tables 1–3, the increase in the total pore volume and internal surface of PIA nanocomposite fibers is connected with increasing the content of variously modified MMT (from 1 to 5%). The highest level of both parameters is shown by fibers containing 5% of the nanoadditive spun at positive values of as-spun draw ratio. The highest total pore volume amounting to 0.944 cm$^3$ g$^{-1}$ and internal surface over 100 m$^2$ g$^{-1}$ are shown by the fibers containing 5% of Nanomer PGW. The values of these parameters and the character of the created porous structure have a bearing on the obtained sorption properties. Generally, the increase in the content of incorporated nanoadditive is accompanied by increased moisture absorption at 100% RH and considerably increased water retention. The level of the sorption parameters obtained depend not only on the porous structure of fibers but also on the type of MMT modifier. The analysis of the porous structure of PIA nanocomposite fibers and their sorption properties is given in previous papers [10–12, 21]. The highest moisture absorption at 100% RH at a level of 15–17% is shown by the fibers containing MMT modified with octadecylamine. At the same time their water retention is high and amounts to 93% for the fibers containing 5% of the nanoadditive. The fibers containing 3% of MMT modified with aminododecane acid are characterized by a moisture absorption of 13.8% and a retention of 53%. When the content of this type of MMT is increased to 5%, the water retention of fibers rises up to 96.7%. Equally high retention, about 100%, is shown by the fibers containing 5% of Nanomer PGW. Their tenacity is decreased by 50% amounting to about 5 cN/tex.

The use of octadecylamine or aminododecane acid to modify MMT do not cause such drastic changes in strength properties. The fibers containing MMT modified with octadecylamine and spun at a negative value of as-spun draw ratio show a tenacity ranging from 15.6 to 13.4 cN/tex. When the nanoadditive content is increased from 1 to 5%, tenacity decreases in succession only by 1 cN/tex. A similar phenomenon takes place in the case of fibers containing MMT modified with aminododecane acid,

but the level of tenacity of fibers containing 1 and 3% of the nanoadditive is lower amounting to 13 cN/tex. The tenacity of PIA nanocomposite fibers (as confirmed by our previous studies [12]) depends not only on the polymer deformability during drawing (being dependent on the nanoadditive content), but first of all on the exfoliation of MMT or its intercalation in the fiber-forming polymer. The lack of complete exfoliation is one of the causes of fiber strength deterioration. The phenomenon of MMT gallery subsidence resulting in their combination and agglomeration, with no good joints between the MMT packages and polymer (no classical intercalation) also causes the strength of fibers containing Nanomer PGW to decrease [9]. At the same time, this facilitates the formation of structure with a higher porosity.

From the thermal analysis it follows that the PIA nanocomposite fibers under investigation contain from 1 to 3.7% of solvent (N-methylpyrrolidone) that is hard to remove, while the content of absorbed water in the examined fibers ranges from 2.5 to 6.2%. The incorporation of 1, 3 or 5% of Nanomer PGW or 1 or 3% of MMT modified with octadecylamine into the fiber-forming polymer generally makes no significant changes in the glass transition temperature ($T_g$) as compared to PIA fibers containing no MMT. It ranges from 280 to 290°C (Fig. 1), while $T_g$ of PIA fibers is included within the range 280–286°C [8]. Lower values of $T_g$ at a level of 260–275°C are shown by the fi-
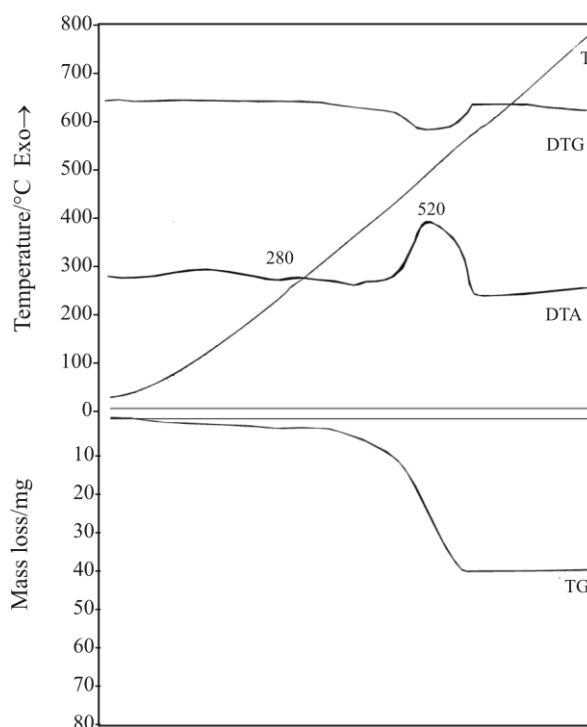


**Fig. 1** TG, DTG and DTA curves of fibers from PIA nanocomposite containing 3% of MMT modified with octadecylamine

**Table 1** Structural parameters and properties of PIA nanocomposite fibres containing Nanomer PGW

| Symbol of sample | Amount of MMT*/ % | As-spun draw out ratio/ % | Total draw ratio/ % | Total pore volume/ cm³ g⁻¹ | Internal surface/ m² g⁻¹ | Moisture absorption at 65% RH/% | Moisture absorption at 100% RH/% | Water retention/ % | Tenacity cN/tex |
|---|---|---|---|---|---|---|---|---|---|
| M 152/1 | 1 | −20 | 115.9 | 0.487 | 63.72 | 6.08 | 9.63 | 82.40 | 11.30 |
| M 152/4 | | +25 | 92.0 | 0.580 | 60.36 | 5.09 | 8.85 | 82.48 | 8.95 |
| M 141/5 | 3 | −20 | 114.7 | 0.633 | 78.92 | 5.62 | 12.20 | 72.00 | 11.55 |
| M 141/2 | | +25 | 123.6 | 0.421 | 53.91 | 5.61 | 12.01 | 72.89 | 12.44 |
| M 153/1 | 5 | −20 | 67.8 | 0.868 | 98.98 | 5.97 | 9.63 | 106.63 | 5.52 |
| M 153/4 | | +25 | 51.2 | 0.944 | 100.99 | 6.00 | 10.30 | 119.90 | 4.98 |

* Amount of MMT is expressed in percentages be wt. in relation to the polymer

**Table 2** Structural parameters and properties of PIA nanocomposite fibres containing MMT modified with aminododecane acid

| Symbol of sample | Amount of MMT*/ % | As-spun draw out ratio/ % | Total draw ratio/ % | Total pore volume/ cm³ g⁻¹ | Internal surface/ m² g⁻¹ | Moisture absorption at 65% RH/% | Moisture absorption at 100% RH/% | Water retention/ % | Tenacity cN/tex |
|---|---|---|---|---|---|---|---|---|---|
| M 156/1 | 1 | −20 | 115.9 | 0.459 | 60.59 | 5.80 | 10.34 | 67.37 | 13.45 |
| M 156/4 | | +25 | 92.0 | 0.553 | 61.27 | 6.02 | 10.96 | 66.12 | 11.85 |
| M 142/10 | 3 | −19 | 123.1 | 0.210 | 35.44 | 6.98 | 12.47 | 22.78 | 13.62 |
| M 142/1 | | +26 | 103.1 | 0.366 | 55.38 | 6.93 | 13.83 | 53.31 | 10.51 |
| M 155/1 | 5 | −20 | 119.8 | 0.425 | 54.53 | 6.02 | 11.39 | 82.56 | 11.08 |
| M 155/4 | | +25 | 83.0 | 0.803 | 88.69 | 6.03 | 10.57 | 96.72 | 9.59 |

* Amount of MMT is expressed in percentages be wt. in relation to the polymer

**Table 3** Structural parameters and properties of PIA nanocomposite fibres containing MMT modified with octadecylamine

| Symbol of sample | Amount of MMT*/ % | As-spun draw out ratio/ % | Total draw ratio/ % | Total pore volume/ cm³ g⁻¹ | Internal surface/ m² g⁻¹ | Moisture absorption at 65% RH/% | Moisture absorption at 100% RH/% | Water retention/ % | Tenacity cN/tex |
|---|---|---|---|---|---|---|---|---|---|
| M 151/1 | 1 | −20 | 145.5 | 0.314 | 48.22 | 4.32 | 11.59 | 63.36 | 15.67 |
| M 151/4 | | +25 | 126.8 | 0.500 | 41.25 | 4.20 | 15.98 | 63.70 | 12.67 |
| M 149/1 | 3 | −20 | 134.0 | 0.517 | 61.31 | 4.40 | 10.09 | 65.54 | 14.06 |
| M 149/4 | | +25 | 116.2 | 0.606 | 72.41 | 4.11 | 10.21 | 63.24 | 12.18 |
| M 154/1 | 5 | −20 | 148.0 | 0.217 | 33.49 | 4.94 | 15.30 | 66.37 | 13.41 |
| M 154/4 | | +25 | 131.7 | 0.711 | 45.24 | 4.69 | 17.23 | 93.39 | 10.45 |

* Amount of MMT is expressed in percentages be wt. in relation to the polymer

bers containing 5% of MMT modified with octadecylamine, which results from the fact that there are no interactions such as Van der Waals' forces between the modifier and the macromolecules of the fiber-forming matter. In this connection one may expect its plasticizing action in the polymeric matrix (the temperature of maximal decomposition rate is 350°C) (Figs 2 and 3), which was previously revealed during the fiber drawing stage. The use of aminododecane acid to modify MMT makes it possible to form secondary bonds between the modifier and polymeric matrix. Therefore, the value of $T_g$ of fibers containing MMT modified with aminododecane acid reaches a slightly higher level of 285–300°C (Fig. 2) depending on the nanoadditive content and fiber porosity. At the same time, higher values of $T_g$ are obtained for the fibers with a lower porosity and higher tenacity spun at a negative as-spun draw ratio. This may be connected with a closer packing of structural elements as well as a better orientation of particular MMT layers along the fiber axis. Based on X-ray measurements (WAXS) of the fibers containing MMT modified with aminododecane acid, the exfoliation of MMT packages in the fiber-forming polymer was found [12], which has a bearing on the development of MMT–polymer contact surface and consequently on a stronger combination of MMT with the polymeric matrix.
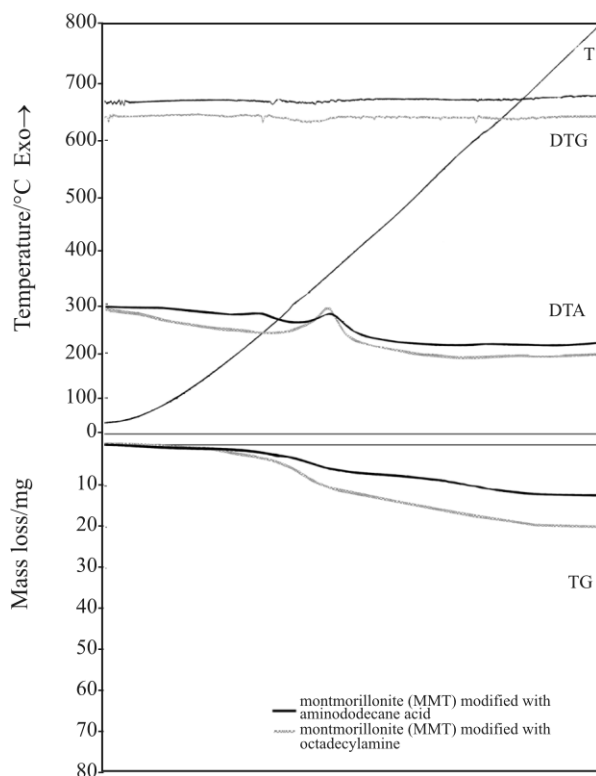
Such a regular relationship is not observed in PIA nanocomposite fibers containing other types of MMT. In their case, there is no exfoliation of MMT packages, while the interlayer distances of MMT are decreased [9, 12], which with their hindered ordering and lower packing density of structural element explains their lower values of $T_g$.

The types of MMT used by us did not cause any increase in the thermal stability ($T_5$ and $T_{50}$) of PIA nanocomposite fibers as compare to PIA fibers without nanoadditive [8] (Table 4). One may assume that the thermal stability of PIA nanocomposite fibers depends on both the thermal stability of fiber-forming polymer and the thermal stability of particular types of incorporated MMT. As follows from Table 5 (Figs 2 and 3), the thermal stability indices of modified MMT depend on the chemical structure of modifier. They are considerably higher when MMT is modified with aminododecane acid. However their values are decidedly lower than the thermal stability of PIA [8].

In this context, the high values of $T_5$ and $T_{50}$ ($T_5$=410°C and $T_{50}$=520°C) (Table 4) in the case of fibers containing 3% (per polymer) of MMT modified with aminododecane acid are probably connected with the exfoliation of MMT packages and increased surface of the MMT–polymer interaction. It should be underlined that these fibers (spun at a negative value of as-spun draw ratio) showed a low total pore volume: 0.2 cm$^3$ g$^{-1}$ and a small internal surface: 35 m$^2$ g$^{-1}$.



**Fig. 2** TG, DTG and DTA curves of MMT modified with aminododecane acid and MMT modified with octadecylamine
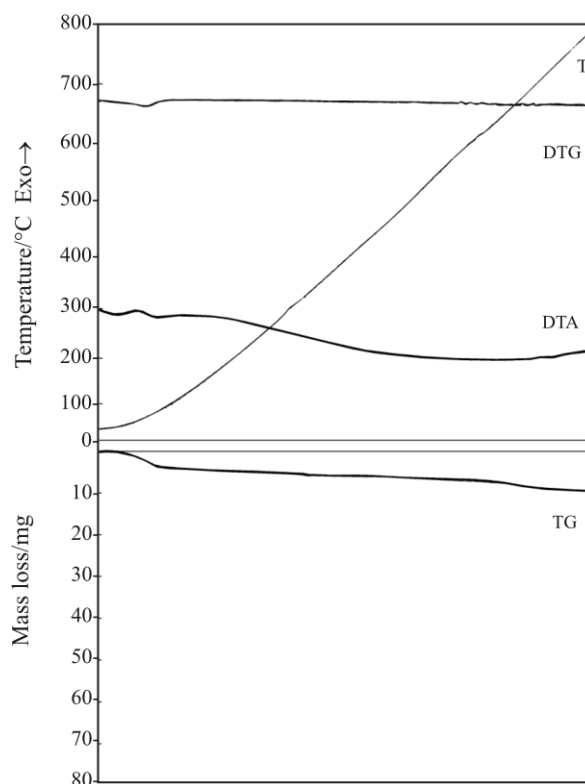


**Fig. 3** TG, DTG and DTA curves of MMT-Na

**Table 4** Thermal properties of fibres from PIA nanocomposite

| Symbol of sample | Type and Mount of MMT in fiber-forming polymer | $Z_z$/% | $Z_R$/% | $T_g$/°C | $T_5$/°C | $T_{50}$/°C | $T_R$/°C | $T_{Rmax}$/°C | $dm/dt/$ mm |
|---|---|---|---|---|---|---|---|---|---|
| M 152/1 | Nanomer PGW 1% | 6.25 | 1.3 | 280 | 390 | 500 | 390 | 515–520 | 28 |
| M 152/4 |  | 5 | 2.6 | 295 | 390 | 515 | 395 | 520 | 26 |
| M 141/5 | Nanomer PGW 3% | 5 | 3.7 | 285 | 410 | 510 | 370 | 515 | 14 |
| M 141/2 |  | 5.5 | 2.5 | 280 | 370 | 500 | 340 | 495 | 12 |
| M 153/1 | Nanomer PGW 5% | 2.5 | 3.5 | 280 | 410 | 515 | 375 | 525 | 21 |
| M 153/4 |  | 2.5 | 1.2 | 290 | 390 | 515 | 400 | 530 | 26 |
| M 156/1 | MMT modified with aminododecane acid 1% | 5 | 2.5 | 295 | 390 | 395 | 370 | 510 | 19 |
| M 156/4 |  | 3.75 | 1.3 | 285 | 390 | 500 | 380 | 515 | 27 |
| M 142/10 | MMT modified with aminododecane acid 3% | 3.7 | 2.5 | 295 | 410 | 520 | 390 | 520 | 10 |
| M 142/1 |  | 3 | 1.6 | 280 | 395 | 505 | 375 | 515 | 12 |
| M 155/1 | MMT modified with aminododecane acid 5% | 6 | 1.25 | 290 | 395 | 510 | 390 | 525 | 24 |
| M 155/4 |  | 5 | 1.3 | 300 | 365 | 510 | 410 | 530 | 26 |
| M 151/1 | MMT modified with octadecylamine 1% | 5 | 1.25 | 285 | 410 | 510 | 375 | 515 | 26 |
| M 151/4 |  | 5 | 2.6 | 280 | 385 | 500 | 410 | 515 | 27 |
| M 149/1 | MMT modified with octadecylamine 3% | 3.7 | 1.25 | 280 | 375 | 500 | 370 | 520 | 13 |
| M 149/4 |  | 6 | 1.25 | 285 | 355 | 505 | 360 | 520 | 16 |
| M 154/1 | MMT modified with octadecylamine 5% | 3.7 | 1.0 | 260 | 390 | 515 | 370 | 525 | 22 |
| M 154/4 |  | 3.75 | 1.3 | 275 | 350 | 500 | 415 | 530 | 23 |

$Z_z$ – adsorbed water content, $Z_R$ – solvent content, $T_g$ – glass transition temperature, $T_5$, $T_{50}$ – thermal stability indicators, $T_R$ – temperature of initial polymer decomposition, $T_{Rmax}$ – temperature of polymer decomposition maximum rate, $dm/dt$ – polymer decomposition rate

The value of polymer initial decomposition temperature ($T_R$) can be affected by the content of MMT as well as the type of its modifier and fiber porosity. As the temperature, at which the decomposition of PIA nanocomposite fibers begins is considerably higher than that of the decomposition of MMT modifier, the effect of the type of modifier on its value may be eliminated. Our studies have shown that the addition of MMT generally increases the temperature of initial thermal decomposition of PIA nanocomposite fibers as compared to fibers containing no MMT [8]. The highest value of this parameter was shown by PIA fibers containing 5% of each type of MMT used. At the same time, these fibers, spun at a positive value of as-spun draw ratio, are characterized by the highest total pore volume (Tables 1–3). Thus, one may assume that the addition of such a high quantity of nanoadditive compensates the disadvantageous influence of porosity on the value of $T_R$ in the initial stage of decomposition. At the beginning of decomposition, the mechanism of dispersed MMT barrier action consisting in cutting off the access of oxygen from surroundings and the pore system seems to be effective. Under the influence of flame, a layer of carbonized polymer is formed on the packages or layers of MMT dispersed in the polymer. It retards the oxygen access and inhibits the oxidation of volatile decomposition

products as well as further flame propagation and polymer decomposition. On the other hand, with rising temperature and advancement of polymer decomposition, the air present in pores is 'released' and the quantity of MMT may be insufficient to eliminate this effect. In the case of fibers containing 1% of MMT, their porosity is smaller by 50% as compared to that of fibers containing 5% of MMT (spun at positive values of as-spun draw ratio). Hence their $T_R$ values are slightly lower ranging from 375 to 410°C as compared to those of fibers containing 5% of MMT (375–415°C), which suggests that the quantity of incorporated MMT was too small.

The temperature of maximal decomposition rate ($T_{Rmax}$) shows an upward trend with increasing the quantities of particular types of MMT from 1 to 5%. In almost all cases (except sample M 141/2), $T_{Rmax}$ ranges from 510 to 530°C, while the highest $T_{Rmax}$ amounting to 530°C is shown by the fibers containing 5% of MMT. The values of $T_{Rmax}$ of fibers containing 3% of various types of MMT are similar ranging from 515 to 520°C (Figs 1 and 4). The relations between fiber porosity, the content of incorporated MMT and the mechanism of its barrier effects are also visible in the values of decomposition rate of particular types of PIA nanocomposite fibers.
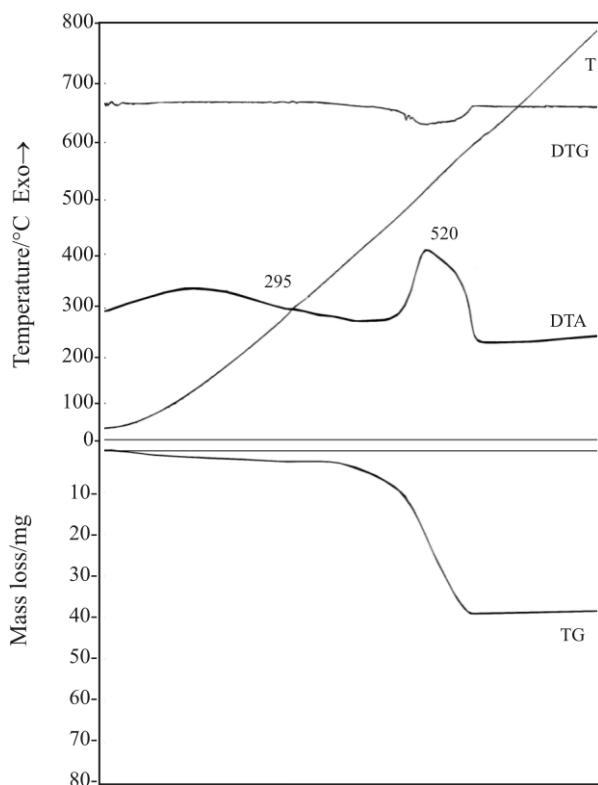
**Fig. 4** TG, DTG and DTAcurves of fibres from PIA nanocomposite containing 3% of MMT modified with aminododecane acid

From the comparison of the decomposition rates of fibers containing 1, 3 and 5% of various types of MMT it follows that higher decomposition rates are observed for the fibers spun at a positive value of as-spun draw ratio, which simultaneously show a higher porosity than that of fibers spun at a negative as-spun draw ratio (Table 4). It is characteristic that the decomposition rate of fibers containing 1 and 5% of MMT is considerably higher than that of fibers containing 3% of MMT. The following explanation of this phenomenon seems to be probable. One may assume that decisive and opposed influence on the decomposition rate is exerted by the MMT content and the total pore volume. It is obvious that the presence of air in empty spaces of the polymer will increase its decomposition rate, while the presence of MMT will retard this action. The 1% MMT content is too low to compensate the disadvantageous influence of porosity. On the other hand, the 5% MMT content is accompanied by almost a double increase in the total pore volume being particularly visible in the fibers spun at a positive value of as-spun draw ratio. Despite the increased MMT content, also in this case the consequences of such a high porosity level have not been compensated.

The situation is different when fibers contain 3% of MMT. Fibers containing all types of MMT in this quantity show considerably lower decomposition rates. At the same time, fibers with such MMT content are characterized by a lower porosity than that of those containing 5% of the nanoadditive. The porosity level (in fibers spun at a positive value of as-spun draw ratio) is similar to that of fibers containing 1% of MMT. One may assume that in this case the disadvantageous effect of porosity on the polymer decomposition rate has been compensated (due to the incorporation of an appropriate quantity of MMT).

Woven fabrics made from fibers containing 3 and 5% of variously modified MMT were tested for flammability. The tests included also an additional sample of woven fabric made from fibers containing MMT modified with aminododecane acid and spun under optimal conditions at a negative as-spun draw ratio (–20%) and lowered deformation during drawing, which made it possible to obtain an increased porosity of 0.41 $cm^3 g^{-1}$ and an internal surface of 58.3 $m^2 g^{-1}$ as well as better sorption properties (moisture absorption at 100% RH: 17.35%, water retention: 60.1%) than those of sample M 142/10.

In accordance with expectations based on the results of thermal analysis, the flammability of fibers is clearly connected with their thermal decomposition rate. The decrease in the thermal decomposition rate reduces the amount of volatile polymer destruction products passing to flame. The woven fabrics made from fibers containing 3% of each MMT type, whose value of $dm/dt$ ranged from 10 to 13 mm (spun at a negative as-spun draw ratio) showed a clearly decreased flammability as compared to that of fibers containing 5% of MMT whose decomposition rate was twice as high (Table 4).

The woven fabrics made from PIA nanocomposite fibers containing 3% of variously modified MMT do not catch fire after 7–8 s of flame action, except fabrics made from fibers containing MMT modified with octadecylamine or aminododecane acid (forming in optimal conditions) which have a slightly shorter time of flame action, 6 s. This is consistent with their higher porosity and internal surface as the air present in the empty spaces of polymer facilitates and accelerates the combustion process.

Generally, the time of flame action of 6–8 s, after which the tested fabric is not ignited, allows one to include the fabrics from PIA nanocomposite fibers containing 3% of variously modified MMT among flame-retardant fabrics.

When the MMT content is increased to 5%, the time of flame action, after which samples are not ignited is however shortened to 2–3 s. Thus, one may assume that despite the increased MMT content, the formed layers of carbonised polymer less efficiently retard the transport of mass and energy between solid and gaseous

**Table 5** Indicators of thermal stability of different types of MMT

| Type of MMT | $T_5$/°C | $P_{800}$/% |
|---|---|---|
| Nanomer PGW | 70 | 37.5 |
| MMT modified with aminododecane acid | 40 | 32.5 |
| MMT modified with octadecylamine | 100 | 47.5 |
| MMT-Na | 40 | 25.0 |

$P_{800}$ – the rest of MMT after heating up to 800°C

phases. Now the increased amount of air in the system of polymer pores caused by the considerably increase total pore volume and internal surface of these fibers has become a decisive factor in this regard.

When the time of flame action is extended to 9–10 s, there appears a phenomenon of consequent burning within 5–11 s for the woven fabric made from fibers containing 3% of Nanomer PGW or MMT modified with aminododecane acid. In the case of MMT modified with octadecylamine this period of time is shortened to 8 s. It is characteristic that this phenomenon does not envelope the whole width of fabric sample, while the flame propagates via two paths aiming at its edges. This is typical and analogous to the formation of paths in the case of gas permeability in polymeric nanocomposites [22–24]. This effect is more visible in fibers containing MMT modified with aminododecane acid, in which the exfoliation of MMT packages is observed. In the case of woven fabric made from fibers containing 5% of various types of MMT, the extension of flame action time to 7 s also results in the consequent burning.

Generally, the effect of the type of MMT modifier and the mode of its dispersion in the fiber-forming polymer on fiber flammability is difficult to assess due to similar values of flame action time, within which the tested fabric sample does not ignite. The suggestion of a beneficial influence of the MMT package exfoliation in the case of its modification with aminododecane acid seems to be confirmed by quite long times of flame action without igniting the fabric made from fibers spun under optimal conditions and showing an increased porosity.

## Conclusions

• The glass transition temperature of PIA nanocomposite fibers depends on the type of MMT modifier. The interactions between modifier molecules and polymer macromolecules make it possible to obtain higher values of $T_g$ of the fibers containing MMT modified with aminododecane acid. In the absence of these interactions (MMT modi-

fied with octadecylamine) the increase in the MMT content results in a lowered $T_g$ due to the plasticizing character of this modifier.
• Due to the thermal decomposition of modifier taking place at a temperature of ~350°C there is no influence of the type of MMT modifier on the thermal stability of PIA nanocomposite fibers defined with parameters $T_5$ and $T_{50}$.
• Irrespective of the as-spun draw ratio used and associated differences in porosity, the highest temperature of maximal decomposition rate is shown by the PIA nanocomposite fibers containing 5% of MMT.
• The MMT content in PIA nanocomposites at a level of 3% made it possible to compensate the disadvantageous effect of porosity on the polymer decomposition rate.
• The flammability test results of woven fabrics made from PIA nanocomposite fibers containing 3% of variously modified MMT allow one to include them among flame-retardant fibers.

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