

Analysis of the Effect of the Amount and Type of Montmorillonite on the Supermolecular Structure, Porosity, and Properties of Polyimidoamide Fibres

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ABSTRACT: The effect of the amount and type of montmorillonite (MMT) on the supermolecular structure, porosity, and properties of polyimidoamide (PIA) fibres has been investigated. An increase in the quantity of nanoadditive incorporated into the fiber-forming polymer from 1 to 5% results in a decrease in the strength properties of fibers. The level of the sorption parameters of PIA nanocomposite fibers depends not only on the nanoadditive content, but also on the type of modifier used to change

the MMT properties from hydrophilic to organophilic. It has been found that the exfoliation of MMT depends on the chemical structure of its modifier. The exfoliation takes place when MMT is modified with aminododecane acid. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1937–1946, 2007

Key words: polyimidoamides; structure; fiber properties; nanocomposites; montmorillonite

INTRODUCTION

The modification of synthetic fibers is possible mainly by changing the chemical structure of the fiber-forming polymer or selecting fiber-spinning conditions so as to obtain the desirable features. This procedure is very useful in the case of fibers spun from the polymer solution by the wet-spinning process.¹ An effective method of modifying fiber properties and imparting new features to fibers is the incorporation of various types of nanoadditives such as nanooxides, carbon nanotubes, and mainly nanoparticles of montmorillonite (MMT).^{2,3} Such an approach has been used by us in the studies on heat-resistant fibers made from a modified polyimidoamide (PIA)⁴ and PIA nanocomposite.⁵ The modification of PIA by incorporation flexible segments derived from diaminodiphenylmethane or diaminodiphenylmoxide^{6–10} into the polymer resulted in an increased polymer susceptibility to deformation during the stage of plasticising drawing. Under selected spinning conditions, this method allowed us to obtain PIA fibers with a high thermal stability⁴ as

well as increased porosity and moisture absorption at the same time. Their tenacity (at a level of 15–16 cN/tex) was suitable for textile processing.

Good sorption properties, especially a high water retention determine the comfort of using the protective clothing designed for the so-called first contact with flame. An increased fiber porosity that accompanies these properties may result in some decrease in the resistance of fibers to the action of heat flux and flame determined on the basis of their flammability. It has become possible to compensate for this disadvantageous effect by the incorporation of dispersed MMT into the modified PIA.⁵ The MMT packages coated with a thin layer of carbonized polymer on their surface act as a barrier that cuts off the access of oxygen and heat flux and consequently limits oxidation of the gaseous products of decomposition. Thus, the fibers obtained from such a nanocomposite show multi-functional properties and a decreased flammability.⁵

It was also expected that the presence of MMT in the fiber-forming polymer would have a beneficial effect on the strength properties of fibers. According to the literature reports,³ nanocomposites containing MMT are characterized mainly by an increased strength, decreased vapor and gas permeability and increased thermal stability.

However, in the case of fiber-forming polymers, the most important factors determining the strength properties of the obtained fibers is the orientation of macromolecules along the fiber axis and the number of secondary bonds formed between them.

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The presence of MMT in the fiber-forming polymer decreases its susceptibility to deformation during the drawing stage. As a result, the tenacity of fibers made from PIA nanocomposite containing 3% of nanomer PGW is lower by 3 cN/tex. This effect depends to a considerable extent on the value of the as-spun draw ratio.¹¹

The strength level of fibers from PIA nanocomposite depends also on the type of MMT dispersion and the MMT-polymer interactions (exfoliation or intercalation). It has been shown¹² that the lower strength of fibers from PIA nanocomposite containing Nanomer PGW (as compared to that of fibers without MMT) is due to the lack of complete exfoliation of MMT packages and the collapse of MMT galleries. On the other hand, such phenomena facilitate the increase in the total pores volume and internal surface of fibers and consequently the absorption of moisture.

The level of strength of PIA nanocomposite fibers is also connected with the type of modifier used to change the MMT properties from hydrophilic to organophilic, compatible with both the solvent and polymer. This effect has been already partly considered^{11,13,14} in terms of variable process parameters for PIA nanocomposite fibers containing 3% of variously modified MMT. The present study was intended to perform a wider examination program including three different weight fractions of MMT: 1, 3, and 5%, modified with various compounds.

The aim of this study was to assess the effect of the type of modifier of MMT and the quantity of incorporated nanoadditive on the supermolecular structure, porosity, and strength properties of PIA nanocomposite fibers. It was also intended to connect the observed changes in the sorption and strength properties of fibers to the type of MMT dispersion (determined by the WAXS method) in the polymer volume.

MATERIALS AND METHODS

PIA fibers containing the following types of MMT were investigated

- MMT–Nanomer PGW, a commercial product from Nanocor.
- MMT modified with aminododecane acid.
- MMT modified with octadecylamine.

Both MMT modified with aminododecane acid or octadecylamine were prepared at the Institute of Industrial Chemistry, Warsaw, under the supervision of Dr. M. Kędzierski. The characteristics of the incorporated nanoadditives are given in papers.^{13,14}

Fibers were spun from postreaction PIA solutions in *N*-methylpyrrolidone. The various types of MMT were incorporated (according to the procedures

given in Ref. 15) in the form of suspension in solvent after being treated with ultrasounds for 60 min at a temperature of 20°C. The concentrations of spinning solutions ranged from 19 to 20%. The intrinsic viscosity of PIA was 1.4 to 1.6 dL/g. The PIA solutions containing MMT modified with aminododecane acid, except the one containing 3% of MMT incorporated without ultrasonic grinding of agglomerates, showed slightly lower values of intrinsic viscosity of about 1.26 dL/g. Detailed characteristics of the rheological properties of spinning solutions containing 3% of nanoadditive are given in paper.^{11,16}

Fibers containing various types of MMT in quantities of 1, 3, and 5% were spun at a selected negative or positive value of as-spun draw ratio to obtain either a higher strength or increased moisture absorption of PIA nanocomposite fibers, respectively.

The term as-spun draw ratio means a ratio of linear velocity of freshly solidified fiber to the average linear velocity of spinning solution in the spinneret capillary. The value of as-spun draw ratio can be higher or lower than 1 or equal to 1; it can be expressed in percent. The type of porous structure depends on the fiber-forming conditions including also the value of as-spun draw ratio. The formation mechanism of capillaries with different sizes and uniformities of their distribution in the fiber cross section has been presented in details for other fiber-forming polymer in paper.¹⁷ Depending on the solvent content in the solidification bath and its temperature, the process can proceed according to the diffusion or drop-wise mechanism.

Fibers were spun from the polymer solution by the wet-spinning process using a laboratory-spinning machine, whose construction made it possible to stabilize the technological parameters at a required level under continuous control. Spinnerets with 240 orifices of a diameter of 0.08 mm were used. The solidification process was carried out in a bath containing an aqueous solution of the solvent (above 55%) at a low temperature, of about 15–18°C. The drawing process was performed in a single stage, in a plasticizing bath containing the same content of solvent as that in the coagulation bath, at an elevated temperature within the range of 65–70°C. Finally, the solvent was rinsed off, and the resultant fibers were dried under isometric conditions.

Moisture absorption at 65 and 100% of relative air humidity was determined by the desiccative method in accordance with Polish Standard PN-80/P-04,635.

Water retention was measured using centrifuge. Fiber 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 for 10 min at an acceleration of 10,000 m/s².

Fiber tenacity and elongation at break were measured in accordance with European Standard PN-EN-

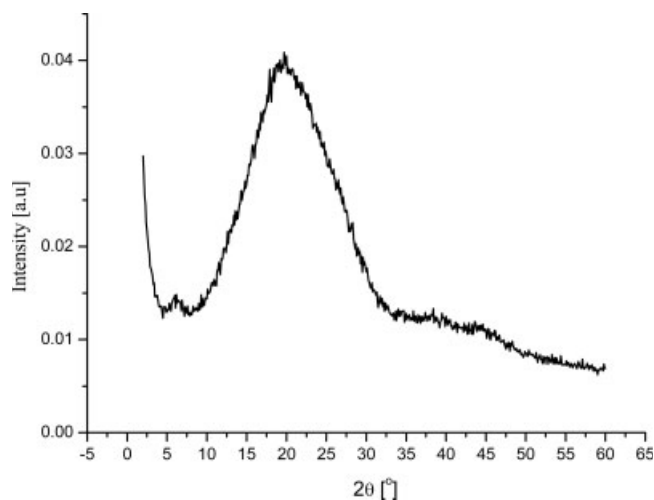


Figure 1 Diffraction curve of fibers made from PIA nanocomposite containing 3% of Nanomer PGW (sample 141/5).

ISO-2062:1997, referring the breaking force to the fiber linear density in tex.

Fiber porosity was measured by means of Carlo-Erba mercury porosimeter, which was linked to a computer system to register the numerical values of the parameters measured. The values measured included the total pore volume, the total internal surface, the volume of the capillary group with a defined radius, and the percentage content. This method allows determining the pore percentage content within given ranges in the total capillary size-range from 5 to 7500 nm.

X-ray measurements were performed by means of URD 6 diffractometer from Seifert (Germany) equipped with a copper X-ray tube, working at supply parameters $U = 40$ kV and $I = 30$ mA. $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) was monochromized with a nickel filter. Diffraction curves were recorded from $2\theta = 2^\circ$ to 60° with a step of 0.1° and from $2\theta = 2^\circ$ to 12° with a step of 0.05° using the symmetrical reflection mode of measurement. The fibers to be measured were powdered by means of a microtome to remove fiber texture and then pressed to obtain tablets with a diameter of about 2 mm and thickness of 1 mm.

RESULTS AND DISCUSSION

The supermolecular structure of fibers is completely amorphous. Their diffractograms show no crystalline peaks. Only two broad amorphous halos are visible (Fig. 1). The first of them is located at $2\theta \approx 20^\circ$ and the other at $2\theta \approx 40^\circ$. Moreover, most of the fibers show a slight reflex deriving from MMT at $2\theta \approx 5^\circ\text{--}6^\circ$.

The structure formed during solidification influences the course of deformation taking place during the plasticizing stage. The use of negative values of as-spun draw ratio under mild solidification conditions is typical for the diffusion mechanism, which makes it possible to form a fine-porous structure and obtain increased mechanical properties of fibers. When the remaining parameters of solidification are constant, the use of positive values of as-spun draw ratio (according to the general principle of spinning highly porous fibers¹) is one of the conditions to obtain fibers with increased porosity and moisture absorption. In the case of PIA nanocomposite fibers, both the strength properties and moisture absorption are also dependent on the quantity of incorporated MMT and the type of its modifier.

From the analysis of sorption properties presented in Tables I–III, it follows that regardless of the type of MMT used, the fibers formed at positive values of as-spun draw ratio are characterized by higher values of moisture absorption at 100% RH and retention, as compared to those ones spun at a negative as-spun draw ratio. On the other hand, the use of negative values of as-spun draw ratio allows one to obtain fibers with a higher tenacity by 1–3 cN/tex, except for fibers containing 3% of Nanomer PGW, whose better strength properties are obtained at positive values of as-spun draw ratio. This may be connected with the fact that in producing these fibers, the MMT agglomerates have not been yet grinded with ultrasounds (prior to the incorporation of their suspension in a solvent into the postreaction solution), and in the case of a large agglomeration of MMT packages, their easier orientation takes place still in the liquid stream.¹¹

TABLE I
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 (cm^3/g)	Internal surface (m^2/g)	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

TABLE II
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 (cm ³ /g)	Internal surface (m ² /g)	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	5.8	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 142/8	3	-19	123.1	0.210	35.44	6.98	12.47	22.78	13.62
M 142/3		+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

The moisture absorption at 100% RH of fibers containing Nanomer PGW ranges from 8.85 to 12.3% depending on the incorporated nanoadditive. The lowest value of this parameter is shown by the fibers containing 1% of Nanomer PGW and the highest values (about 12%) by those containing 3% of this nanoadditive. These results are consistent with the character of the created porous structure. The content of small pores (Table IV) in the fibers containing 3% of MMT spun at a positive value of as-spun draw ratio is the highest and amounts to 31.3% as indicated by one of the highest maxima within the range of small pores (Fig. 2) in the plot of pore size distribution, which maintains a bimodal character. The formation of porous structure of such a character may be connected with the fact that the presence of large agglomerates is likely to limit the formation of pores with large dimensions.

The dimensions of small pores facilitates the moisture absorption through capillary condensation, which has a bearing on higher moisture absorption (12%) and lower retention (72%) (Table IV). The highest retention, exceeding 100%, is shown by the fibers containing 5% of Nanomer PGW spun at a negative as well as a positive value of as-spun draw ratio. This is consistent with the high contents of large and medium pores in the end portion of their range (Table IV), with the total pores volume being very high, at a level of 0.86–0.94 cm³/g. The internal surface of these fibers is also high, amounting to 100 m²/g (Table I).

Generally, an increase in the content of incorporated Nanomer PGW from 1 to 5% results in a con-

siderable increase in both the total pore volume and internal surface. However, this is accompanied by a significant decrease in fiber tenacity from 11–12 cN/tex for fibers containing 1 and 3% of the nanoadditive to 5.5 cN/tex for fibers containing 5% of MMT (Table IV). This effect may be connected with a small extent of exfoliation of the aluminosilicate layers and collapse of MMT galleries, which has been already observed in fibers containing 3% of this nanoadditive.¹²

In the WAXS diffractograms of all the fibers containing Nanomer PGW, the 2θ angle, at which appears the reflection from MMT, is about 6.2°; thus it is almost twice as high as that from the hydrophobized MMT prior to its incorporation into the polymeric matrix (about 3.4°) (Fig. 3). This means that after incorporation into the matrix, the basal spacing of the MMT structure has decreased from 25.8 to 14.3 Å and consequently, the distance between the layers has decreased from 15.8 to 4.3 Å (the thickness of aluminosilicate layers is about 10 Å). Hence, the collapse of galleries result in the formation of clusters, within the volume of polymeric matrix, consisted of very closely packed aluminosilicate layers which unlike individual exfoliated layers and intercalated laminar systems are weakly connected with the polymeric matrix. That is why the mechanical properties of nanocomposite are deteriorated. On the other hand, because of the weak connection with the matrix, these clusters bring about a considerable increase in fiber porosity and the formation of small and medium-sized pores.

TABLE III
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 (cm ³ /g)	Internal surface (m ² /g)	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

TABLE IV
Characteristic of Porous Structure PIA Nanocomposite Fibres
Containing Nanomer PGW

Symbol of sample	As-spun draw out ratio (%)	Percentage pore content (%)			
		Small (4–12.3 nm)	Medium (15–75 nm)	Large (150–750 nm)	Very large (1875–7500 nm)
1%					
M 152/1	–20	26.93	58.34	12.18	2.56
M 152/4	+25	20.01	62.07	15.18	2.76
3%					
M 141/5	–20	23.92	63.16	9.57	3.36
M 141/2	+25	31.36	40.67	18.64	9.32
5%					
M 153/1	–20	22.58	63.14	13.37	0.92
M 153/4	+25	20.33	58.05	17.8	3.81

This is particularly noticeable in the fibers containing 5% of MMT (Table I) which show exceptionally high values of the total pores volume and internal surface, with fiber tenacity being very low at the same time. Figure 3(a,b) shows the diffractograms of M141/5 and M153/1 fibers containing 3 and 5% of Nanomer PGW, respectively.

The PIA nanocomposite fibers containing MMT modified with aminododecane acid are characterized by a slightly higher moisture absorption at 100% RH as compared to that of fibers containing Nanomer PGW (Table II). The highest value of this parameter, about 12–13%, is shown by the fibers containing 3% of nanoadditive. Also in their making, similarly as in the case of fibers with a 3% content of Nanomer PGW, MMT agglomerates were not grinded with ultrasounds. Such high values of moisture absorption at 100% RH are consistent with the still higher content of small pores, exceeding 43% (Table V), as indicated by the high maximum in the plot of pore size distribution (Fig. 4) within the range 4–11 nm. At the same time, the bimodal character of the distribution function has been maintained. However, the

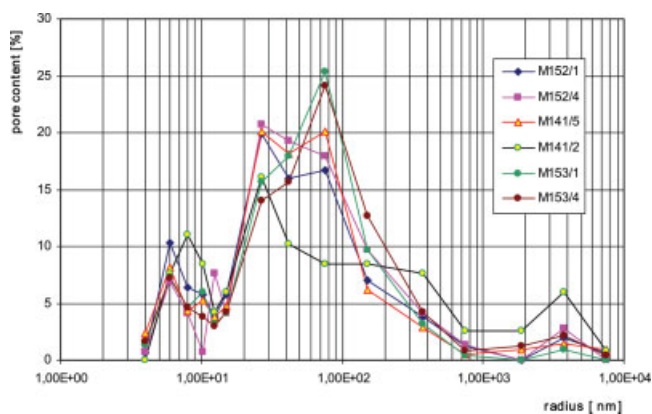


Figure 2 Size distribution of pores for fibers made from PIA nanocomposite containing Nanomer PGW. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

second maximum within the range of medium pores was considerably lowered as compared to that of fibers containing Nanomer PGW, which resulted in a lower level of retention, especially in the case of fibers containing 3% of MMT. Also relatively lower, but still at a high level 82–96.7%, are the values of

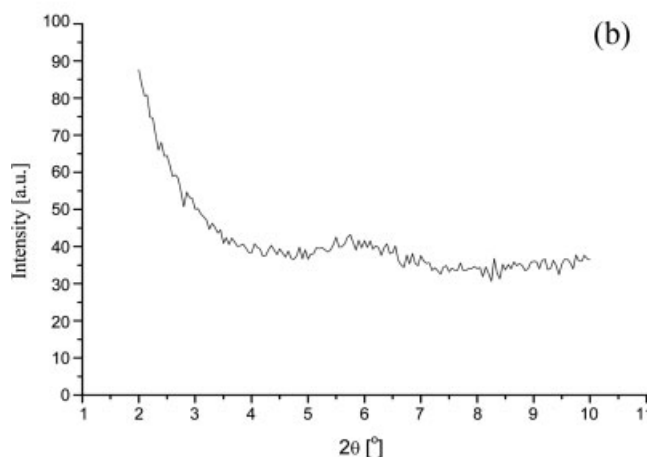
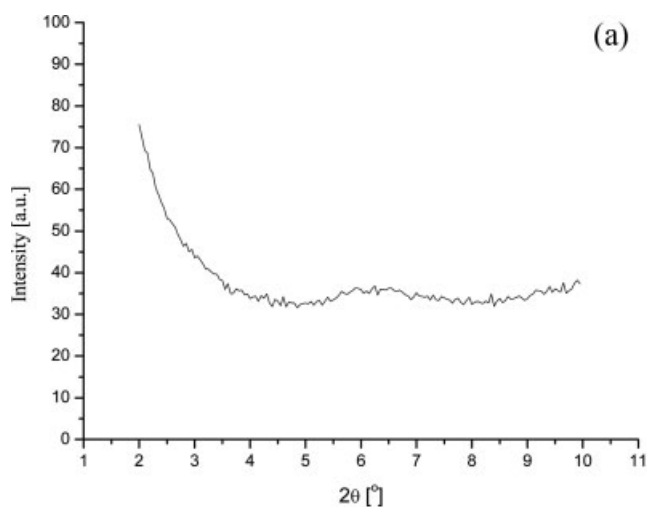


Figure 3 Diffraction curves for fibers M 141/5 (a) and M 153/1 (b), containing 3 and 5% of Nanomer PGW, respectively.

TABLE V
Characteristic of Porous Structure PIA Nanocomposite Fibres Containing MMT
Modified with Aminododecane Acid

Symbol of sample	As-spun draw out ratio (%)	Percentage pore content (%)			
		Small (4–12.3 nm)	Medium (15–75 nm)	Large (150–750 nm)	Very large (1875–7500 nm)
1%					
M 156/1	−20	27.42	58.07	12.1	2.42
M 156/4	+25	23.23	45.81	22.59	8.39
3%					
M 142/8	−19.64	64.29	19.04	7.14	9.52
M 142/3	+26.2	43.19	28.41	19.32	9.1
5%					
M 155/1	−20	26.53	59.84	10.61	3.03
M 155/4	+25	9.64	62.26	13.65	3.62

retention of fibers containing 5% of MMT modified with aminododecane acid (Table II). On the other hand, in the case of fibers containing Nanomer PGW, an increase in the nanoadditive content has not caused such a considerable deterioration in the fiber strength. The tenacity of PIA nanocomposite fibers containing 1 and 3% of MMT modified with aminododecane acid, spun at a negative value of as-spun draw ratio, amounts to 13.6 cN/tex and that of fibers with 5% nanoadditive content is 11.08 cN/tex (Table II). Most likely, such a high level of tenacity is possible due to the fact that the exfoliation of MMT proceeds in these fibers to a considerably larger extent than that in the case of fibers containing Nanomer PGW. This is confirmed by the considerably weakening or almost complete disappearing of the reflection from MMT, in WAXS diffractograms of those fibers, in which MMT is modified with aminododecane acid. Examples are shown on Figure 5 (a,b). It should be emphasized, that the positive effect of MMT on the strength parameters of polymeric nanocomposites, reported in the literature,^{18–21} is connected just with the exfoliation of MMT pack-

ages and the dispersion of aluminosilicate layers in the polymer volume. Another reason, in the case of the fibers under consideration, is a possible formation

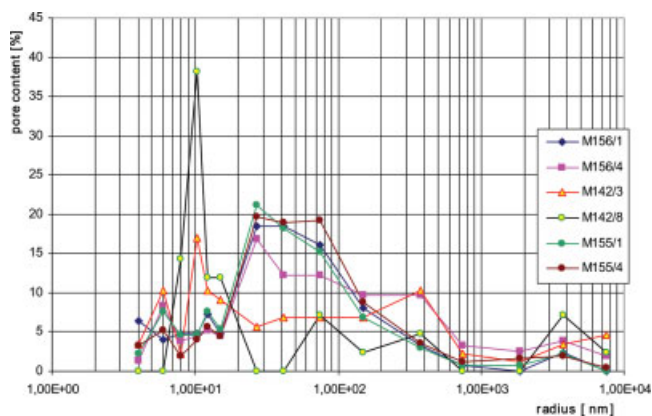


Figure 4 Size distribution of pores for fibers made from PIA nanocomposite containing MMT modified with aminododecane acid. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

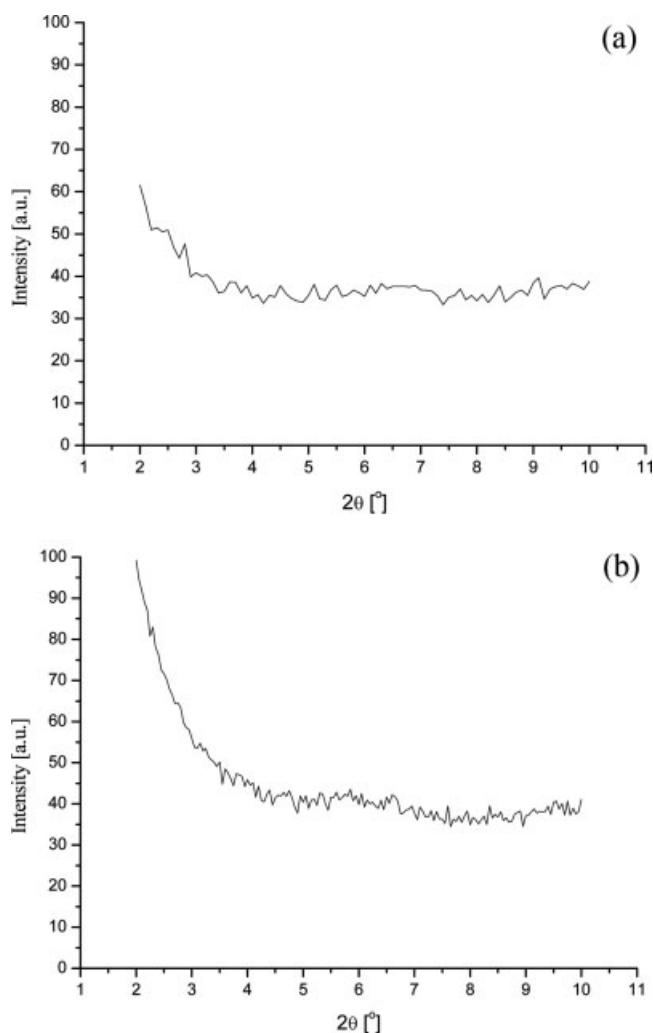


Figure 5 Diffraction curves for fibers M 142/8 (a) and M 155/1 (b), containing 3 and 5% of MMT modified with aminododecane acid respectively. Fibers were formed without the stage of grinding of MMT with ultrasounds.

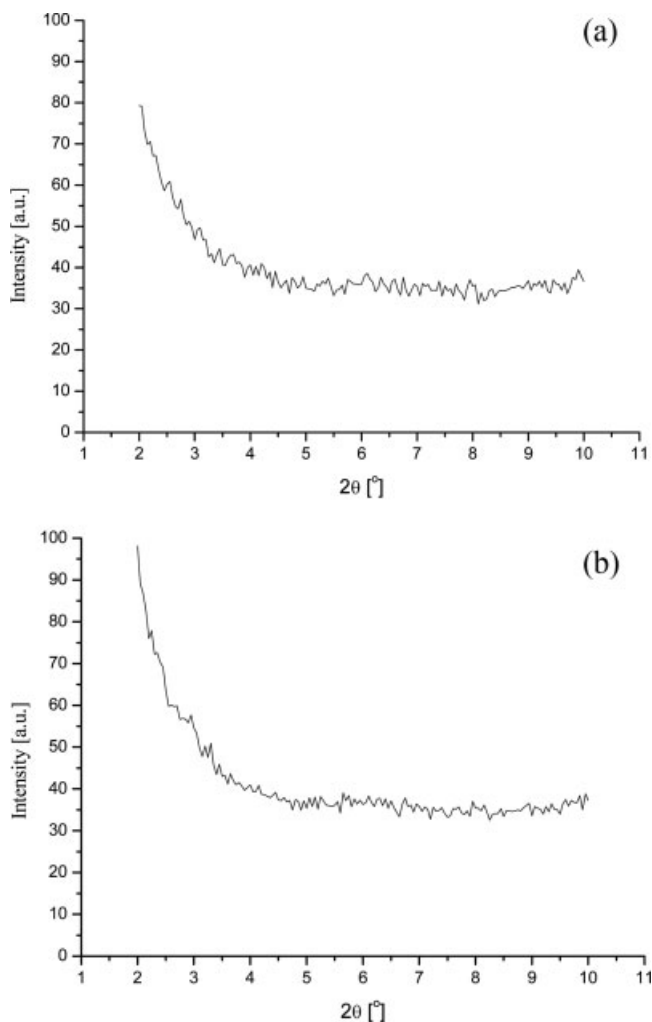


Figure 6 Diffraction curves for fibers M 157/1 (a) and M 157/4 (b), containing 3 and 5% of MMT modified with aminododecane acid, respectively. Fibers were formed with the stage of grinding of MMT with ultrasounds using 20% (a) and +25% (b) as-spun draw ratio, respectively.

of additional secondary bonds between amide groups of PIA and acidic groups of the MMT modifier. Performed investigations have shown that the ultrasonic grinding of MMT agglomerates prior to the addition of MMT dispersion to the PIA solution also influences the internal structure of the nanocomposites. The WAXS diffractograms of the fibers, which have been produced with the use of the ultrasonic treatment stage, show a complete decay of the reflection from MMT [Fig. 6(a,b)], which suggests even higher extent of exfoliation than that in the fibers made without this additional stage. This means that in the case of MMT modified with aminododecane acid, the ultrasonic grinding of MMT agglomerates facilitates further decomposition of the MMT packages into individual aluminosilicate layers.

The PIA nanocomposite fibers containing 1 and 5% of MMT modified with octadecylamine are

characterized by the highest values of moisture absorption at 100% RH from among all the examined fibers. In the case of fibers containing 5% of the nanoadditive, spun at a positive as-spun draw ration, the value of this parameter exceeds even 17%. This is consistent with the character of the pore size distribution (Fig. 6) which shows high maxima within the range of small and medium pores. At the same time, the total pores volume is high (Table III), amounting to $0.7 \text{ cm}^3/\text{g}$ and the internal surface exceeds $45 \text{ m}^2/\text{g}$. Similarly as in the case of the fibers described earlier, the plots of pore size distribution maintain their bimodal character. A lower moisture absorption at 100% RH, about 10.2%, is shown by the fibers containing 3% of nanoadditive, whose maxima in the pore size distribution within the range of small pores are also lower (Fig. 7), while the percentage contents of these pores do not exceed 27% (Table VI). Pores with such dimensions are capable of absorbing moisture by capillary condensation. A relatively high values of water retention of 63–66% are connected with the considerable content of pores from the terminal portion of the medium and large range of pores. Pores with such dimensions are capable of water absorption and retention even after a mechanical removal.

Similarly as the fibers containing Nanomer PGW and MMT modified with aminododecane acid, also the fibers containing 5% of MMT modified with octadecylamine, spun at a positive as-spun draw ration, show the highest values of moisture absorption at 100% RH and retention (Table III).

The moisture absorption at 65% RH of fibers containing various types of MMT depends on the type of MMT modifier. Comparable absorption values of 5–7% are shown by the fibers containing Nanomer PGW and MMT modified with aminododecane acid (Tables II and III). The lower values of this parameter, 4.1–4.9%, of the fibers containing MMT modified

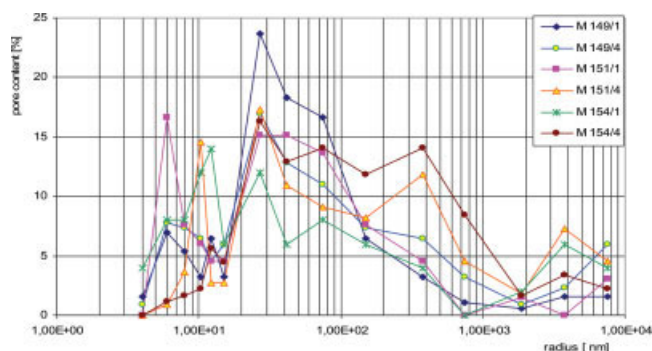


Figure 7 Size distribution of pores for fibers made from PIA nanocomposite containing MMT modified with octadecylamine. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VI
Characteristic of Porous Structure PIA Nanocomposite Fibres Containing MMT Modified with Octadecylamine

Symbol of sample	As-spun draw out ratio (%)	Percentage pore content (%)			
		Small (4–12.3 nm)	Medium (15–75 nm)	Large (150–750 nm)	Very large (1875–7500 nm)
1%					
M 151/1	–20	34.86	48.49	12.13	4.55
M 151/4	+25	21.83	40.0	24.55	13.64
3%					
M 149/1	–20	23.66	61.84	10.76	3.76
M 149/4	+25	27.07	46.78	16.97	9.17
5%					
M 154/1	–20	46.0	32.0	10.0	12.0
M 154/4	+25	10.68	47.74	34.27	7.31

with octadecylamine (Table III) are connected with the fact that this modifier has no groups capable of forming hydrogen bonds with water molecules. The PIA nanocomposite fibers containing MMT modified with octadecylamine, similarly as those with MMT modified with aminododecane acid, maintain their good strength properties even with the nanoadditive content increased to 5%. The tenacity of the fibers spun at a negative value of as-spun draw ratio ranges from 15.6 to 13.4 cN/tex and is the highest from among all the three types of PIA nanocomposite fibers. However, the WAXS diffractograms of this third group of fibers show clear reflections coming from MMT, which indicates that the exfoliation proceeds here to a small extent. The reflections appear at the angle $2\theta \approx 5.7^\circ$ – 5.8° , which means that similarly as in the fibers containing Nanomer PGW, also in these fibers, the collapse of galleries takes place in the MMT packages [Fig. 8(a,b)]. Consequently, clusters are formed, composed of closely packed aluminosilicate layers. As follows from Bragg's law, this time the distances between layers are higher and amount to about 5.3 Å. Hence, there is a possibility of slightly better connection of clusters with the polymeric matrix than that in the fibers containing Nanomer PGW. However, it is rather not possible for this effect, to be the major reason of better strength parameters of these fibers. The most probable cause is their more ordered and less defected structure. Such a structure was formed owing to the higher deformations reached during drawing, which was facilitated by the better dispersion of MMT resulted from the treatment of the nanoadditive with ultrasounds. Moreover, the collapsing of galleries in the MMT packages is accompanied with the penetration of octadecylamine, partially released from among the aluminosilicate layers, into the polymer matrix. Because of its chemical structure, the octadecylamine does not form secondary bonds with the matrix and thanks to this, acts as a plastificator favoring higher deformations of the fibers.

A comparison of the total pores volume in particular groups of fibers containing 1, 3, and 5% of the

nanoadditive respectively, shows, that this parameter reaches the lowest value in the fibers containing MMT modified with octadecylamine (Tables I–III), except for the fibers containing 3% of MMT modified

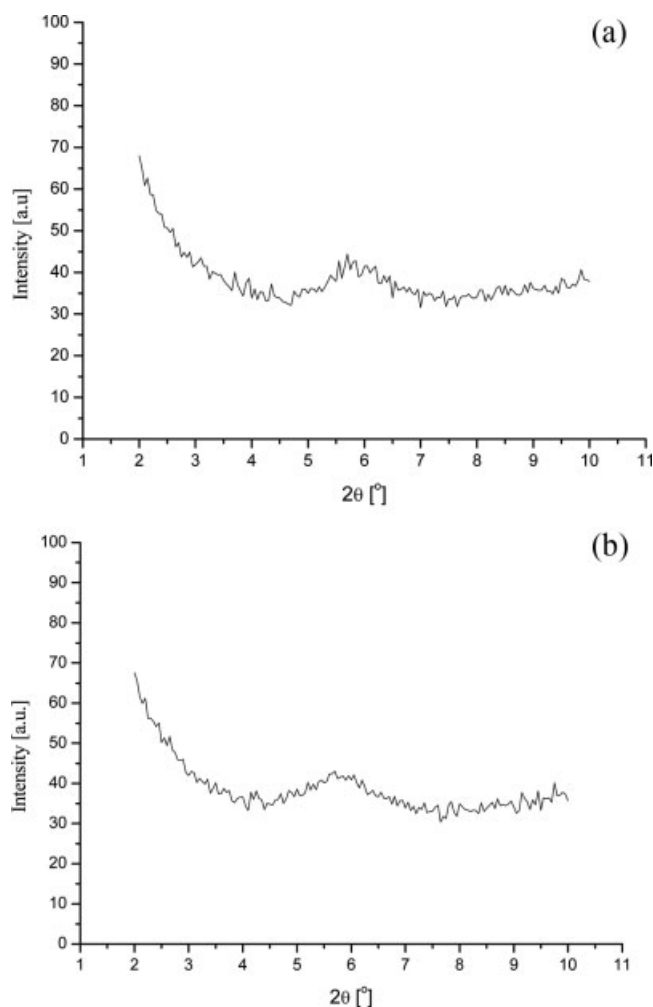


Figure 8 Diffraction curves for fibers M 149/1 (a) and M 154/1 (b) containing 3 and 5% of MMT modified with octadecylamine respectively.

with aminododecane acid. However, in the case of the latter fibers, the comparison is made difficult due to the fact that unlike the fibers containing MMT modified with octadecylamine, they were made without the ultrasonic grinding of MMT agglomerates. Their lower strength, with simultaneously low porosity, could be due to the presence of large MMT clusters in the fiber volume.

The comparative analysis of the effect of the type of MMT incorporated into the fiber-forming polymer (PIA) presented above indicates, that considering the aim of the study consisting in making fibers with increased porosity, moisture absorption, and tenacity at the same time, the use of nanoadditive in the form of Nanomer PGW is the least beneficial. Both the fibers containing MMT modified with aminododecane acid and octadecylamine are characterized with better strength properties. They maintain their good and suitable for textile processing strength properties even with an increased nanoadditive content up to 5%. In the case of fibers containing MMT modified with aminododecane acid, this has become possible owing to the exfoliation of MMT packages into isolated aluminosilicate layers. It should be noticed that this phenomenon takes place only in the fibers of that group. Thus, one may assume that it is connected with the chemical structure of modifier and its interaction in the polymer-solvent system used. On the other hand, good strength properties of fibers containing MMT modified with octadecylamine are connected mainly with the formation of a more ordered structure, resulting from a better susceptibility to deformation during the drawing stage. The easier course of deformation processes and higher values of draw ratio were possible thanks to the good grinding down of MMT agglomerates by the ultrasonic treatment and thanks to the plastificating action of octadecylamine released from the collapsed MMT packages. By lowering the value of the total draw ratio of fibers containing 3% of this nanoadditive (spun at a negative value of as-spun draw ratio) it was possible to increase fiber porosity and moisture absorption. Such fibers are characterized by the total pore volume over $0.5 \text{ cm}^3/\text{g}$ and internal surface of $61.3 \text{ m}^2/\text{g}$, which allows us to classify them as fibers with increased porosity. Such a structure, with predominating quantities of medium-sized pores, ensures high water retention, over 65%, and good sorption properties. Their tenacity at a level of $14.06 \text{ cN}/\text{tex}$ is suitable for textile processing.

CONCLUSIONS

1. An increase in the quantity of nanoadditive incorporated into the fiber-forming polymer from 1 to 5% results in a decrease in the strength properties of fibers. This decrease is particularly high for fibers containing 5% of Nanomer PGW and much lower, by about 1–1.5 cN/tex, for the remaining PIA nanocomposite fibers.
2. An increase in the nanoadditive content is accompanied by an upward trend in the total pores volume and internal surface of the fibers spun at a positive value of as-spun draw ratio. The related changes in sorption properties are also dependent on the character of the porous structure formed.
3. The level of the sorption parameters of PIA nanocomposite fibers depends not only on the nanoadditive content, but also on the type of modifier used to change the MMT properties from hydrophilic to organophilic.
4. The strength properties of PIA nanocomposite fibers depend not only on the polymer susceptibility to deformation during drawing, possible formation of secondary bonds between polymer macromolecules and modifier, but also on the exfoliation of MMT in the fiber-forming polymer and on the fiber porosity.
5. The exfoliation of MMT depends on the chemical structure of its modifier. The exfoliation takes place when MMT is modified with aminododecane acid. The use of ultrasounds to grinding down MMT agglomerates results in a considerable increase in the extent of exfoliation.
6. Among the PIA nanocomposite fibers under investigation, the fibers containing 3% of MMT modified with octadecylamine are characterized by the best strength properties (tenacity at a level of $14 \text{ cN}/\text{tex}$) and at the same time showing high porosity and excellent sorption properties, especially high retention (about 65%).

References

1. Mikołajczyk, T. Modification of the manufacturing process of polyacrylonitrile fibres, *Scientific Bulletin of Technical University of Lodz*, No. 781, Scientific Theses Z 243, Łódź, 1997.
2. Kacperski, M. *Polimery (Warsaw)* 2002, 47, 801.
3. Sinha Ray, S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
4. Janowska, G.; Mikołajczyk, T. *J Therm Anal Calorim* 2003, 71, 549.
5. Janowska, G.; Mikołajczyk, T.; Olejnik, M. *J Therm Anal Calorim*, to appear.
6. Mikołajczyk, T.; Janowska, G.; Urbaniak-Domagala, W.; Szczapińska, M. *Fibres Text East Eur* 2004, 12, 27.
7. Mikołajczyk, T. *Fibres Text East Eur* 2002, 10, 52.
8. Mikołajczyk, T.; Skwarski, T. *Fibres Text East Eur* 2002, 10, 52.

9. Mikołajczyk, T.; Skwarski, T. *Fibres Text East Eur* 2002, 10, 14.
10. Skwarski, T.; Ratajczyk, J.; Mikołajczyk, T. *Fibres Text East Eur* 2002, 10, 35.
11. Mikołajczyk, T.; Olejnik, M. *J Appl Polym Sci* 2006, 100, 3323.
12. Mikołajczyk, T.; Rabiej, S.; Olejnik, M.; Urbaniak-Domagala, W. *J Appl Polym Sci* 2007, 104, 339.
13. Mikołajczyk, T.; Olejnik, M. *J Appl Polym Sci* 2006, 101, 1103.
14. Mikołajczyk, T.; Olejnik, M. *J Appl Polym Sci* 2007, 103, 2940.
15. Mikołajczyk, T.; Olejnik, M. *Fibres Text East Eur* 2005, 13, 24.
16. Mikołajczyk, T.; Olejnik, M. *Fibres Text East Eur*, submitted.
17. von Falkai, B. *Syntesefasern-Grundlagen, Technologie, Verarbeitung und Anwendung*; Verlag Chemie: Weinheim, 1981.
18. Bharadwaj, R. K. *Macromolecules* 2001, 34, 9189.
19. Delozier, D. M.; Orwoll, R. A.; Cahoon, J. F.; Johnston, N. J.; Smith, J. G., Jr.; Connell, J. W. *Polymer* 2002, 43, 813.
20. Agag, T.; Koga, T.; Takeichi, T. *Polymer* 2001, 42, 3399.
21. Liang, Z.; Lin, J.; Xu, H. *Polymer* 2003, 44, 1391.