Strength Properties of Polyimideamide Nanocomposite Fibers in Terms of their Porous and Supermolecular Structure

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ABSTRACT: The strength properties of fibers made from polyimideamide (PIA) nanocomposite were investigated and the effect of the presence of MMT in the fiber-forming polymer on the porous structure and supermolecular structure of fibers was analyzed. It was found that lower strength properties (tenacity, elongation at break) of PIA nanocomposite fibers, as compared with those ones of fibers without montmorillonite (MMT), are connected with a lower deformability of the polymer during drawing stage and the collapse of MMT galleries, confirmed by WAXS investigations. This results in the formation of agglomerates that are weakly connected with the fiber-forming polymer. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 339–344, 2007

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

INTRODUCTION

Nanocomposites, owing to their unique properties, are more and more often used in the production of polymeric materials. Improved or new properties of these materials can be obtained by the incorporation of some quantities, maximum up to 7%, of a nanoadditive into the polymeric matrix, while maintaining good processing behavior of the fiber-forming polymer.[1]

The most often used components of both thermoplastic[2] and thermosetting[3] polymeric nanocomposites are nanoparticles of layered silicates (MMT) and silica.

MMT-containing nanocomposites show better strength and thermal properties, reduced flammability,[1] as well as lower vapor and gas permeability. This is due to a specific layer structure of MMT, being a hindrance to the penetration of gases, and the elongation of their path of diffusion. The flammability is reduced because of the formation of carbonized polymer layers on the surface of MMT. Hence, a barrier to the access of oxygen is formed, which reduces the oxidation of gaseous combustion products. An increase in tensile strength of MMT-containing nanocomposites is associated among others with the formation of strong interfacial interactions between MMT and polymer matrix, e.g., secondary bonds in PA6, between amide groups and oxygen atoms of MMT.[1] Moreover, a large interface between all exfoliated MMT layers and polymer can consider-

ably reduce the formation of shear zone and stop the evolution from the shear zone to cracks.[4]

In the case of fibers, the strength properties also depend on the orientation of macromolecular chains along the fiber axis and on the number of secondary bonds formed between them. In both cases, the phenomena of intercalation or exfoliation of MMT in the polymer matrix are of great importance. On the other hand, the presence of a nonfiber-forming nanoadditive exerts a negative effect on the fiber deformability and consequently on the strength properties of fibers spun from solution by the wet process.[5]

Hence, it should be expected that in the case of PIA nanocomposite fibers investigated in this study obtained level of strength will be the resultant of all of the factors mentioned above.

The modification of PIA consisting in the incorporation of flexible segments derived from diaminedi-phenylomethane[6] or diaminediphenylooxide[7] into the macromolecule chain resulted in an increase in the fibers deformability during the plasticizing drawing. A proper selection of spinning conditions resulted in the production of fibers with increased porosity, good sorption properties, and tenacity amounting to 15 cN/tex,[8] on the stage of plasticizing drawing. At the same time, the fibers did not lose their good thermal properties.[9] These features are of importance when the fibers under discussion are designed for protective clothing of so-called first contact with flame, as they increase their comfort of use.

The incorporation of MMT into PIA resulted in the improvement in the resistance to flame (based on

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TABLE I
Characteristics of the Spinning Solution of Polyimidoamide Containing MMT in *N*-methylpyrolidone
and Modified Polyimidoamide

Symbol of solution	Concentration of spinning solution [%]	Intrinsic viscosity [η] [dl/g]	Apparent dynamic viscosity [Pas]	Rheological parameters	
				n	k
Nanocomposite PIA M141	19.78	1.63	30.95	0.9948	29.576
Nanocomposite PIA M140	19.78	1.80	33.33	0.9684	34.36
Modified PIA	19.20	1.20	21.43	0.98	35.76

flammability test), increase in porosity and sorption properties of the obtained fibers. However, the tensile strength was slightly decreased.[10,11] To explain this phenomenon, WAXS investigations were performed aimed at the determination of the internal structure of nanocomposites in terms of intercalated, flocculated, or exfoliated arrangement of MMT in the polymer matrix.

The aim of the present study was to assess the effect of the incorporated nanoadditive, its arrangement in the fiber-forming polymer, as well as the influence of as-spun draw out ratio and fiber deformation during drawing on the structural parameters and strength properties of PIA nanocomposite fibers.

CHARACTERISTICS OF MMT AND SPINNING SOLUTION

In accordance with previously performed studies, a modified montmorillonite, Nanomer PGW (a commercial product of Nanocor, USA), in the form of suspension in a solvent was added to postreaction solutions after terminating the synthesis, followed by heating for a constant time at a predetermined temperature.[12]

The characteristics of polymer and spinning solution are given in Table I.

FIBER SPINNING

Fibers form PIA nanocompisite 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.

METHODS

Moisture absorption at 65 and 100% relative air humidity was determined by the desiccator method according to Polish Standard PN-71/P-04,635.

Water retention was measured by the centrifuge method. 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 off for 10 min at an acceleration of 10,000 m/s^2.

Fiber tenacity and elongation at break were measured according to the Polish Standard PN-85/P-04,761/04, 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 interval surface, the volume of capillary group with a defined radius, and percentage content. This method allows one to determine the pore percentage content with given ranges in the capillary set with size of 5–7500.[9]

X-ray measurements were carried out with the use of an URD 6, Seifert diffractometer (Germany) equipped with a copper target X-ray tube ($\lambda = 1.54$ Å), operated at: U = 40 kV and I = 30 mA. The radiation was monochromized by means of a nickel filter. Diffraction curves were recorded using the symmetrical reflection method and the step mode of measurement. The angular range of recording was from $2\theta = 2°$ to 60°, with a step of 0.1° and from $2\theta = 2°$ to 12°, with a step of 0.05°. The investigated fibers were powdered by a microtome to eliminate fiber texture and then pressed into pills with the diameter of about 2 cm and thickness of 1 mm.

RESULTS AND DISCUSSION

The properties of fibers depend on the structure formed during the stage of solidification and its deformability during drawing. The basic parameter influencing the value of the longitudinal rate gradient is the as-spun draw out ratio. As it follows from previous studies,[10] the use of positive values of as-spun draw out ratio is

TABLE II
Structural Parameters and Properties of Fibers from PIA Nanocomposite and Fibers from Modified PIA

Symbol of sample	As-spun draw out ratio [%]	Total draw ratio [%]	Total pore volume [cm³/g]	Internal surface [m²/g]	Moisture absorption at 65% RH [%]	Moisture absorption at 100% RH [%]	Water retention [%]	Tenacity [CN/tex]	Elongation [%]
M141/5	−20	114.6	0.633	78.92	5.2	10.4	70.0	11.55	12.8
M141/4	−5	108.6	0.753	80.68	5.6	12.0	72.9	10.67	7.2
M141/3	+10	110.1	0.478	76.94	5.6	11.3	65.4	11.89	8.5
M141/2	+25	123.6	0.421	53.91	5.3	11.1	70.0	12.44	7.9
M141/1	+50	96.1	0.586	59.75	5.6	12.2	72.0	11.36	8.2
M140	−20	127	0.440	55.53	6.2	13.26	76.22	10.77	15.53
W$_1$	20.3	128.3	0.29	32.26	4.5	11.0	58.50	15.00	15.9

beneficial to the fiber spinning from PIA nanocomposite. This allows one to create proper conditions of deformation of a still liquid stream of solidifying polymer and orientation of MMT dispersed inside it, along the fiber axis. There is also a better possibility to form secondary bonds between amide groups of the polymer and oxygen atoms of MMT.

The investigations performed in this study show that the highest tenacity, at a level of 11.3–12.5 cN/tex, is reached by the fibers spun with positive values of as-spun draw out ratio: +25% and +50% (Table II). Their refractive index for light polarized in the plane parallel to the fiber axis also reaches one of the highest values (Table III). These facts confirm a positive influence of liquid polymer stream deformation on the ordering of MMT layers in the polymer volume. The refractive index for light polarized in the plane perpendicular to the fiber axis changes very slightly with an increase in as-spun draw out ratio. As follows from Table II, both the fibers made from the modified PIA (sample W$_1$) and from PIA nanocomposite are optically positive. They have high values of both the longitudinal ($n_\parallel \sim 1.73$) and transverse refractive indices ($n_\perp \sim 1.638$ and $n_\perp \sim 1.650$, respectively). These high values are connected with the chemical structure of fiber-forming polymer, especially with the aromatic

rings present in the PIA macromolecule. The presence of MMT in the fiber-forming polymer causes a slight increase in the n_{II} index and a slightly clearer increase in the transverse refractive index, $n_\perp$. As a result, the birefringence of fibers is decreased. An increase in the index $n_\perp$ is most likely connected with a parallel orientation of MMT layers with respect to the fiber axis, causing a decrease in the velocity of light wave polarized in the plane perpendicular to this axis. In the case of light wave polarized parallel to the fiber axis, the presence of MMT layers that are parallel to the fiber axis also causes a decrease in the velocity (index $n_\parallel$ increases), but it is lower since in this case a decisive influence on the wave velocity is exerted by the chains of polymer macromolecules oriented along the fiber axis.

The fibers formed with positive values of as-spun draw out ratio show a total pore volume of above 0.42 cm³/g and a large internal surface, which justifies their qualification as fibers with increased porosity. The scanning electron microscopy observations of the fibers made from modified PIA (Fig. 1) as well as from PIA nanocomposite (Fig. 2) showed that their porous structure is in the size scale of the order of >0.1 µm.

TABLE III
Values of Refractive Index for Light Polarised in the Plane Parallel or Perpendicular and Index of Birefringence of Fibers from PIA Nanocompisite and Fibers Made from Modified PIA

Symbol of sample	Refractive index for light polarised in the plane parallel or perpendicular		Index of birefringence of fibers ($n_\parallel - n_\perp$)
	$n_\parallel \pm \delta n_\parallel$	$n_\perp \pm \delta n_\perp$	
M 140	1.730 ± 0.002	1.649 ± 0.002	0.081
M 141/1	1.739 ± 0.002	1.653 ± 0.002	0.086
M 141/2	1.736 ± 0.002	1.649 ± 0.002	0.087
M 141/3	1.739 ± 0.002	1.650 ± 0.002	0.089
M141/4	1.737 ± 0.002	1.650 ± 0.002	0.087
M 141/5	1.735 ± 0.002	1.651 ± 0.002	0.084
W$_1$	1.732 ± 0.002	1.638 ± 0.002	0.094
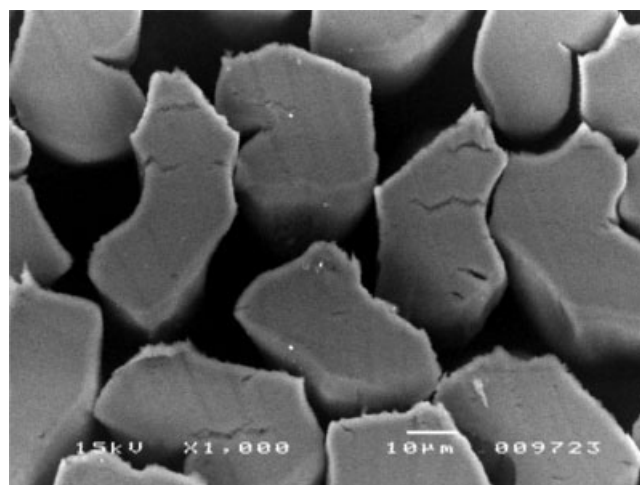
Figure 1 Scanning electron microscope image of fibers from modified PIA.
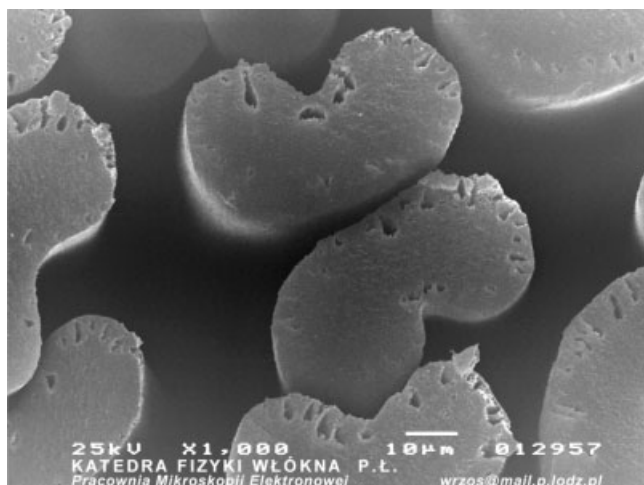
Figure 2 Scanning electron microscope image of fibers from PIA nanocomposite.

A well-developed porous structure, high values of specific surface, and total pores volume of the investigated fibers result in their good, as for a hydrophobic polymer, sorption properties (moisture absorption at 100% RH over 11%) and especially a high water retention, over 70%. A general regularity is also observed[13] that fibers with higher strengths show a lower overall porosity.

Generally, however, the tenacity level of PIA nanocomposite fibers obtained with the process parameters used in this study is lower by 3–5 cN/tex in comparison with that of the fibers made from modified PIA spun under optimal conditions (sample W_1). It should be noted that in the case of fibers made from the modified PIA (without MMT), the use of negative values of ASDO ratio, with the remaining parameters of solidification (temperature and coagulation bath composition) being the same, was beneficial to their tenacity. Meanwhile, the MMT-containing fibers formed with the same value of as-spun draw out ratio and similar deformation during drawing (sample M140) show a higher porosity and tenacity lower by 4.2 cN/tex.

The reasons of deterioration in the tenacity of fibers can be explained based on the results of WAXS investigations. WAXS diffraction pattern of MMT used in this study is shown in Figure 3. The strong peak at the angle of 3.42° is related to the periodicity of layered MMT structure. Using Bragg's law one can calculate that the basal spacing of this structure is equal to $d = 25.8$ Å. This value is the sum of the thickness of aluminosilicate layer amounting to 1 nm[1,14] and the height of gallery between layers filled with an organic modifier. According to the producer (Nanocor), prior to the replacement of sodium ions, the basal spacing of MMT-Na was about 12.3 Å. This means that the distance between aluminosilicate layers increased from about 2.3 Å up to 15.8 Å, owing to the modification. Thus, the access of the polymer to the gallery has become considerably easier.

The incorporation of MMT into the polymeric matrix resulted in a considerable decrease in the peak height and its position. For all examined composite fibers, independently of the parameters of as-spun draw out ratio and other spinning parameters, this peak is located at the same angle $2\theta = 6.23°$ and has the same shape and height. Exemplary diffraction patterns for some fibers are shown in Figure 4.

A dramatic drop in the peak height indicates, as a result of mixing with polymer solution, a part of ordered MMT layer systems is exfoliated, i.e., the layers are dispersed in polymer volume. Another possible effect that could also cause observed drop in the peak height is a considerable distortion of the parallel arrangement of aluminosilicate layers in stacks and related disappearance of periodicity. Such an effect may be caused by an intensive penetration of polymer macromolecules between the layers (intercalation). Nevertheless, despite the decrease in its height, the peak does not disappear completely, showing that apart from dispersed layers, the ordered, stacked MMT systems are still present in polymer volume. However, the peak position is shifted toward higher angles, indicating that the basal spacing of these systems decreases to about 14.2 Å and is only slightly higher than that one in unmodified MMT-Na. This is of course due to a sudden drop in the height of galleries between aluminosilicate layers which decreases from 15.8 Å to 4.2 Å. Thus, a collapse of the layer structures takes place, which means that organic modifier from interlayers is released.

A similar phenomenon has already been reported in literature.[4,15,16] It was found that thermal stability of organic modifiers based on ammonium cations containing long aliphatic chains is relatively low. As a result, they decompose during thermal treatment at high temperature and may be released from the galleries.
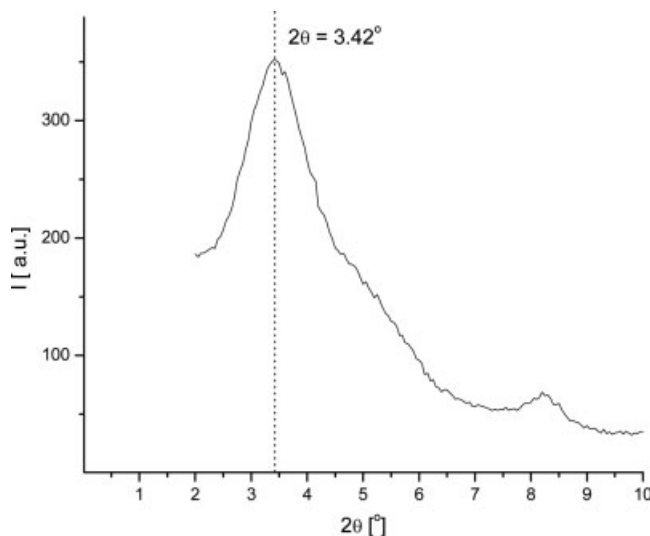
Figure 3 Diffraction curve for MMT.
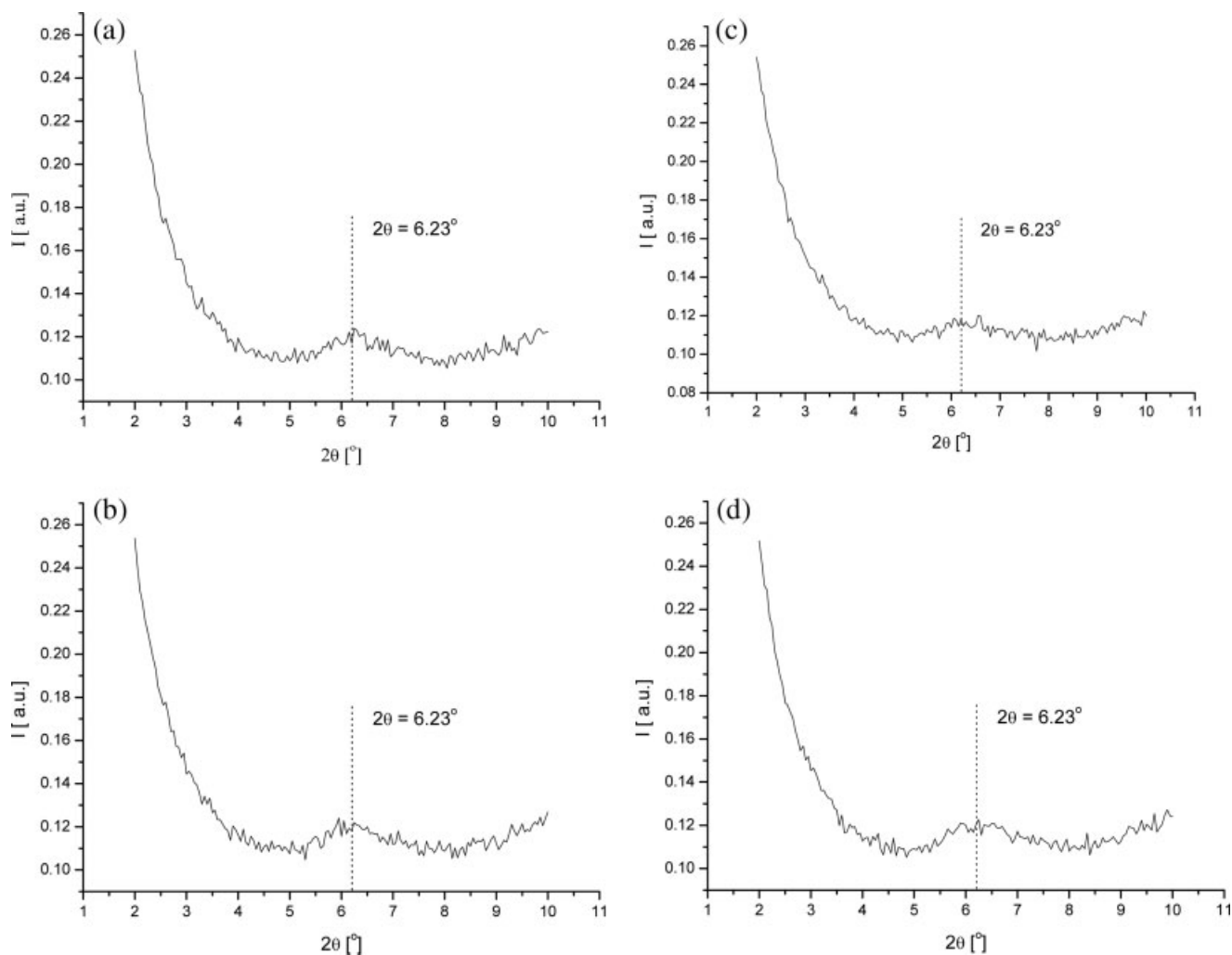
Figure 4 (a) Diffraction curve for the sample M 141/1. (b) Diffraction curve for the sample M 141/2. (c) Diffraction curve for the sample M 141/4. (d) Diffraction curve for the sample M 141/5.

However, the temperatures occurring in the process of fibers formation from PIA nanocomposite were relatively low. Both during the addition of MMT dispersion in a solvent to the postreaction solution as well as in the stage of fiber formation, the temperatures did not exceed 100°C, so they were lower than those at which thermal decomposition of modifier was observed in the papers mentioned above.[4,15,16] Thus, such a decomposition is of considerably smaller importance in the case of investigated fibers, although it cannot be completely excluded. A more probable reason of the collapse of aluminosilicate layers in MMT contained in the postreaction solution of PIA seems to be the interaction between strongly polar molecules of solvent used for the preparation of MMT dispersion and the ions of modifier. This interaction can result in the solvation of ions and consequently in the breaking of bonds between modifier ions and aluminosilicate layers and finally in their migration beyond the interlayer galleries. However, such a scenario does not exclude a limited penetration of PIA macromolecules

as well as solvent molecules, which seems to be even more probable, into these regions. Such a possibility is suggested by the final height of galleries, 4.2 Å, which is slightly higher than before the organophilic modification. The results obtained in this study confirm that the stability of organomodifiers poses a significant problem in the case of nanocomposites made from polymers that require either a high-temperature treatment or the use of polar solvents. The collapse of galleries results in the formation of larger agglomerates in polymer volume which undoubtedly exert a considerable influence on the internal structure and properties of fibers made from the nanocomposite. Big amount of such agglomerates is probably the main reason of decreased tensile strength of the fibers. First of all, the formation of agglomerates excludes exfoliation and homogeneous dispersion of aluminosilicate layers in the fiber-forming polymer. Because of smaller surface to volume ratio, the interfacial interactions between agglomerates and PIA matrix are much weaker, than in the case of individual, exfoliated layers. The agglom-

erates are also weaker connected with polymeric matrix than intercalated MMT systems, in which polymer chains penetrate inside the interlayer galleries. Thus, they are the most disadvantageous type of nanofiller in terms of mechanical properties. On the other hand, because of their weak links with polymer matrix, the agglomerates result in a considerable increase in the fibers porosity and particularly in the formation of relatively large pores. This is consistent with observed increase in the total volume of pores in PIA nanocomposite fibers, especially middle-sized and large pores, as compared with the fibers containing no nanoadditive.[10] The remaining parameters of solidification process (composition and temperature of coagulation bath) were the same for both types of fibers, promoting the solidification occurring in accordance with the diffusion mechanism and resulting in fine-porous structure.

Thus, one can suppose that the strength properties of fibers made from PIA nanocomposite are determined mostly by the polymer deformability, which has been reduced because of the presence of a non-fiber-forming additive. Such a hypothesis is fully confirmed by a considerable drop in the tensile strength of PIA nanocomposite fibers which contain an addition of MMT (Nanomer PGW), increased to 5%. The tenacity of fibers formed under the same conditions as sample M141/5 is 5.52 cN/tex. At the same time, the water retention is considerably increased up to about 106.6%, with the moisture absorption at 100% RH, being still at the similar level about 10%.

SUMMARY

The strength properties of PIA nanocomposite fibers depend on the polymer deformability during the drawing stage as well as on the formation of secondary bonds between PIA macromolecules and MMT layers. However, a disadvantageous effect of the non-fiber-forming additive was compensated only to a small extent, by the creation of these bonds.

Considering sorption properties, the incorporation of MMT into the fiber-forming polymer results in a desired increase in porosity and internal surface of PIA nanocomposite fibers. However, this is accompa-nied by a decrease in fiber strength as compared with that one of fibers without MMT.

Such a negative influence of the nanoadditive on the strength properties of fibers is due to the fact that in the portion of layered MMT systems, the organic modifier is removed from the galleries separating aluminosilicate layers, resulting in their collapse and consequently in the formation of agglomerates which are weakly connected with polymer matrix.

An increase in the refractive index for the light wave polarized in the plane perpendicular to a fiber axis, observed in fibers formed with positive values of as-spun draw out ratio, indicates on a positive influence of the liquid polymer stream deformation on the parallel orientation of MMT layers with respect to this axis.

References

1. Sinha Ray, S.; Okamoto, M. Prog Polym Sci 2003, 28, 1597.
2. Kacperski, M. Polimery (Warsaw) 2002, 47, 801.
3. Kacperski, M. Polimery (Warsaw) 2003, 48, 85.
4. Liang, Z.; Lin, J.; Xu, H. Polymer 2003, 44, 1391.
5. Mikołajczyk, T.; Boguń, M.; Kowalczyk, A. Fibres Text East Eur 2005, 13, 30.
6. Skwarski, T.; Ratajczyk, J.; Mikołajczyk, T. Fibres Text East Eur 2002, 10, 35.
7. Mikołajczyk, T.; Janowska, G.; Urbaniak-Domagała, W.; Szczapińska, M. Fibres Text East Eur 2004, 12, 27.
8. Mikołajczyk, T. Fibres Text East Eur 2002, 10, 52.
9. Janowska, G.; Mikołajczyk, T. J Therm Anal Cal 2000, 71, 549.
10. Mikołajczyk, T.; Olejnik, M. J Appl Polym Sci, to appear.
11. Janowska, G.; Mikołajczyk, T.; Olejnik, M. J Therm Anal Cal, submitted.
12. Mikołajczyk, T.; Olejnik, M. Fibres Text East Eur 2005, 13, 24.
13. Mikołajczyk, T. Modification of the Manufacturing Process of Polyacrylonitrile Fibres, Scientific Buletin of Technical University of Lodz, No 781, Scientific Theses Z 243, Łódź 1997.
14. Bharadwaj, R. K. Macromolecules 2001, 34, 9189.
15. Delozier, D. M.; Orwoll, R. A.; Cahoon, J. F.; Johnston, N. J.; Smith, J. G., Jr.; Connell, J. W. Polymer 2002, 43, 813.
16. Agag, T.; Koga, T.; Takeichi, T. Polymer 2001, 42, 3399.