Effects of Spinning Conditions on Structure and Properties of Multifunctional Fibers of Polyimidoamide Nanocomposites

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ABSTRACT: The effects of basic fiber-forming parameters on the porous structure, moisture absorption, and strength properties of fibers from polyimidoamide nanocomposites were examined. Beneficial fiber-forming conditions were established in consideration of the fiber sorption and strength properties. It was found that the incorporation of montmorillonite into the fiber-forming polymer resulted in beneficial increases in fiber porosity and internal surface area. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3323–3331, 2006

Key words: polyimidoamide; fibers; nanocomposites; rheology

INTRODUCTION

Because of their chemical composition, polyimidoamide fibers, which simultaneously provide barriers to the actions of heat flux and flames (LOI = 30), show thermal resistance comparable to that of polyimide or aramide fibers.[1] These features allow these fibers to be used for textile purposes, mainly in protective clothing of so-called first contact with flames and decorative fabrics in public facility buildings. The good electroinsulating properties of these fibers additionally extend the range of their technical applications.[2]

The major advantage of polyimidoamide fibers is that they emit very little smoke and practically no toxic decomposition products during their contact with flames. Synthesis of fiber-forming polymers is environmentally friendly, and the only byproduct of the polycondensation process, trimellite anhydride with aromatic diisocyanates, is readily removable with CO_2. The postreaction solution can be directly used to spin fibers using the wet process.[3]

Modification of fiber-forming polymer by the addition of flexible segments derived from diamine or diaminediphenyl oxide[2,4–6] increases the susceptibility of polymer to deformation and makes it possible to obtain, even after plasticizing drawing, fibers with a tenacity suitable for textile processing and high thermal stability.[7] The incorporation of montmorillonite (MMT) nanoparticles into such a modified polymer makes it possible to obtain fibers of polyimidoamide nanocomposites characterized by the dispersion of intercalated MMT in the fiber-forming material, which contains polymer macromolecules within the interlayer spaces (Fig. 1).

Because of its composition, sodium aluminosilicate shows hydrophilic properties. To be compatible with the reaction medium, it should be made organophilic by modification with proper compounds, mostly quaternary amines or acids with long aliphatic chains. Such a modification is accompanied by increasing interlayer distances, which facilitate the penetration the interlayer spaces by monomer molecules or polymer macromolecules.[8]

The development of PIA nanocomposite fibers makes it possible to impart several new features generally connected with nanocomposites to these fibers, such as increased tenacity, thermal resistance, decreased gas permeability, and decreased flammability,[8] or to improve the already existing properties connected with the composition of PIA.

Studies of nanosilica-containing fibers made from other fiber-forming polymers have shown[9] that the incorporation of nanoparticles leads to increased fiber porosity and moisture absorption. This feature is important for heat-resistant protective clothes, as it provides improved comfort of use, extending the functional use of the resultant fibers.

The aim of the present work was to assess the effect of basic fiber-forming parameters on the porous structure, sorption, and strength properties of fibers made from PIA nanocomposites and to establish to what

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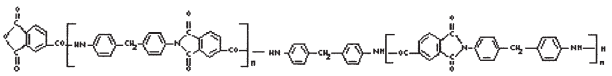

Figure 1 Formula of modified fiber-forming polyimidoamide.

extent these properties depend on the incorporated nanoaddition.

It was assumed that the incorporation of montmorillonite into modified polyimidoamide would increase fiber porosity and moisture absorption. At the same time, fiber tenacity, after the plasticizing drawing stage, should be at a level suitable for good textile processing.

The formation of additional secondary bonds between the macromolecules of modified PIA (with a greater number of amide groups) and the intercalated montmorillonite in this polymer should compensate for the disadvantageous effect of the incorporated non-fiber-forming nanoaddition, as polymer deformability is considerably limited in connection with the rigid structure of polymer macromolecules.

The increased tenacity of fibers made from the polyamide 6 nanocomposite[10] has been found to result from the formation of secondary bonds between the amide groups of polymer macromolecules and the oxygen atoms of montmorillonite.

The use of a computer-aided experimental design system will make it possible to establish process conditions for the manufacture of fibers with optimal sorption and strength properties. For fibers spun from solution by the wet process, there is, in principle, an opposite tendency from the effect of the basic process parameters on the changes in both the above features.[11]

EXPERIMENTAL

Measuring methods

Moisture absorption at 65% and 100% relative air humidity was determined by the desiccator method according to Polish Standard PN-71/P-04635.

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 Polish Standard PN-85/P-04761/04, referring the breaking force to the fiber linear density in tex.

Fiber porosity was measured with a Carlo-Erba mercury porosimeter that was linked to a computer system to register the numerical values of the parameters measured, which included total pore volume, total interval surface, and volume of the capillary group with a defined radius and percentage content. This method allowed the pore percentage content to be determined with the given ranges in the capillary set with a size of 5–7500.[7]

TABLE I
Characteristics of Spinning Solution of Polyimidoamide Containing MMT in *N*-Methylpyrolidone

Symbol of solution	Concentration (%)	Intrinsic viscosity, η (dcl/g)	Apparent dynamic viscosity (Pa s)	Rheological parameters	
				n	k
M-141	19.78	1.63	30.95	0.9948	29.576

Characteristics of montmorillonite and spinning solution

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

The interlayer distance, determined on the basis of the position of the first peak in the X-ray diffraction patterns found by the WAXS method, was 2.3 nm. The dimensions of the MMT lamellae, determined from the scanning electron microscope images, were 800 $\times$ 550 nm.[12] The characteristics of the spinning solution are given in Table I.

The rheological properties of the spinning solution were measured with the use of a Rheostat RV rotary rheometer at a temperature of 20°C, using an H cylinder. The shearing rate ranged between 0 and 50 s^{-1}.

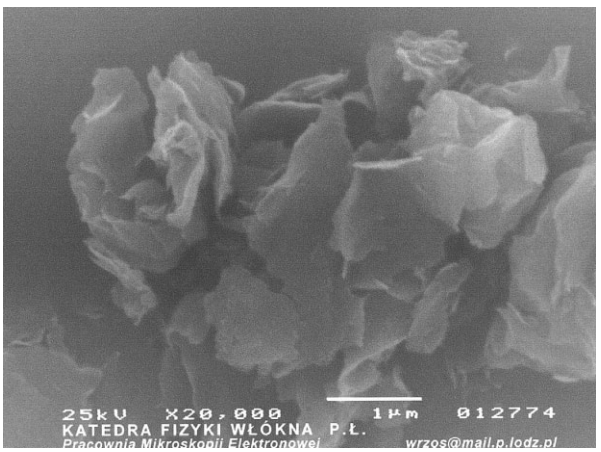

Figure 2 Scanning electron microscope image of montmorillonite (MMT).

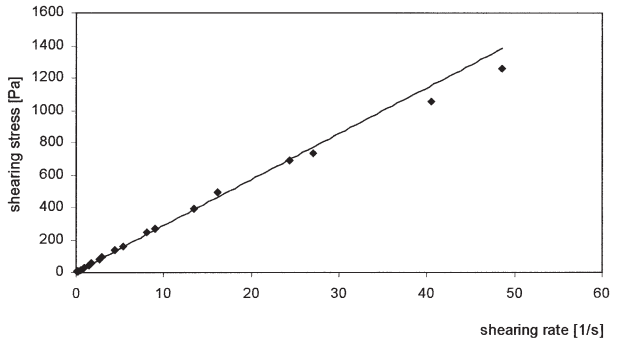

Figure 3 Flow curves of postreaction solutions.

On the basis of the results obtained, a flow curve for the given spinning solution was drawn (Fig. 2). From the analysis of that curve, it followed that the examined solution was a non-Newtonian fluid rarefied by shearing without a flow limit. Confirmation of this came from the flow curve passing the origin of the coordinates and the shearing stress increasing less than proportionally with the increasing shearing rate. The rheological parameters n and k were determined for the examined solution. The value of parameter n was less than unity, which is typical of polymeric fluids of this type. The apparent dynamic viscosity decreased with increases in the shearing rate (Fig. 3).

The rheological properties of solutions of modified polyimidoamide without nanoadditive in *N*-methylpyrrolidone were measured previously.[13]

Fiber spinning

Fibers were spun from solution by the wet process using a laboratory spinning machine whose construction made it possible to stabilize technological parameters at a required level under continuous control. Spinnerettes with 240 orifices 0.08 mm in diameter were used. The solidification process was carried out in a bath containing an aqueous solution of the solvent (above 55%) at low temperature, about 15°C−18°C. The drawing process was performed in a single stage

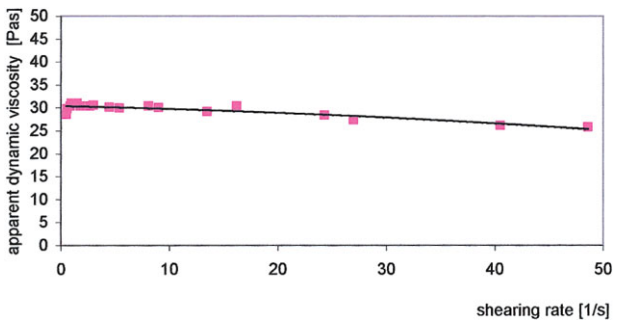

Figure 4 Dependence of apparent dynamic viscosity on the shearing rate.

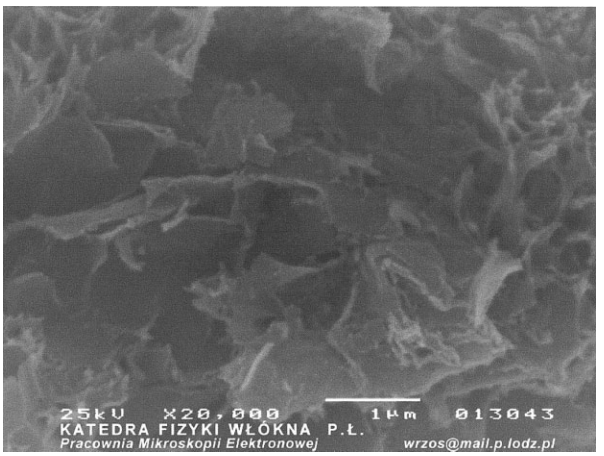

Figure 5 Scanning electron microscope image of PIA fibers with MMT.

in a plasticizing bath containing the same content of solvent as that in the coagulation bath at an elevated temperature of 65°C–70°C. Finally, the solvent was rinsed off, and the resultant fibers were dried under isothermal conditions at 80°C−120°C.

Object of study

Under investigation were fibers made from block polyimidoamide nanocomposites. The content of dispersed montmorillonite in the fiber-forming polymer was confirmed by the images from the scanning electron microscope. The photographs clearly show particular lamellae of intercalated MMT (pictures 2 and 3). The fourth photograph shows the pore structure of fibers that have radial spaced pores externally.

RESULTS AND DISCUSSION

Fiber properties depend on the structure formed during solidification. The composition of the coagulation

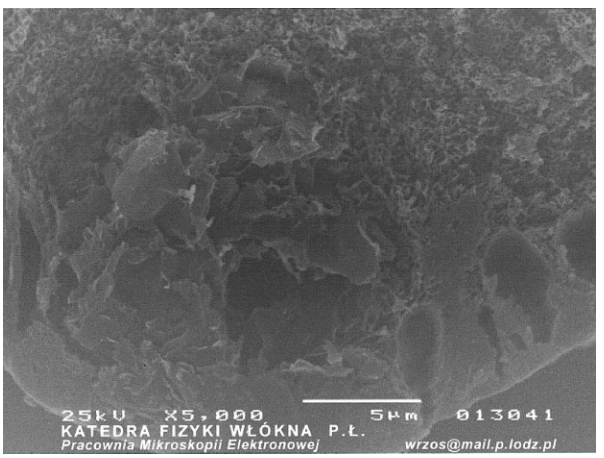

Figure 6 Scanning electron microscope image of PIA fibers with MMT.

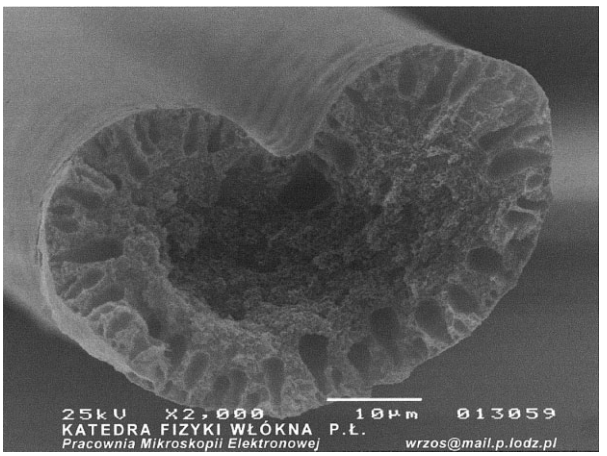

Figure 7 Scanning electron microscope image of PIA fibers with MMT.

bath and its temperature are decisive factors in the course of the solidification process according to the diffusion or dropwise mechanism.[10] Assuming the formation of a fine-porous structure (typical of the diffusion mechanism) that would allow the improved strength properties of fibers to be determined, the solidification process was carried out under mild conditions at a low temperature ranging from 15°C to 18°C in a bath with an up to 55% increased solvent content. A variable parameter was the as-spun draw-out ratio, and related to it was deformation during the drawing stage. The as-spun draw-out ratio varied over a wide range from negative to positive values: −20% to 50%.

From the analysis of sorption properties (Figs. 4 and 5), it follows that the changes in moisture absorption at 100% RH and retention versus the as-spun draw and total draw ratios were similar. The highest values of both the parameters were obtained with negative values, −5%, and extremely positive values of the as-spun draw-out ratio. These values were 12%–12.2% and 72%–72.9%, respectively. Moisture absorption at 65% RH varied within a narrow range of 5.3%–5.6%, showing the same character of being dependent versus both process parameters. The changes in the fiber sorption properties, which were dependent on the porous structure, were generally consistent with the tendency of changes in the total pore volume (Fig. 6) versus the as-spun draw-out and total draw ratios, but within the range of positive values of the as-spun draw-out ratio, the increase in the total pore volume was considerably lower than it would be with increased moisture absorption. On the other hand, the internal surface area of the fibers showed a downward tendency with an increasing as-spun draw-out ratio (Fig. 7). Thus, it can be believed that the sorption properties of fibers depend to a great extent on the percent content of capillaries with different diameters.

The order of magnitude of sorption properties of the fibers from polyimidoamide nanocomposite was generally higher than that of fibers without montmorillonite intercalated in the polymer and spun under the same conditions.[4] This is connected with a higher total

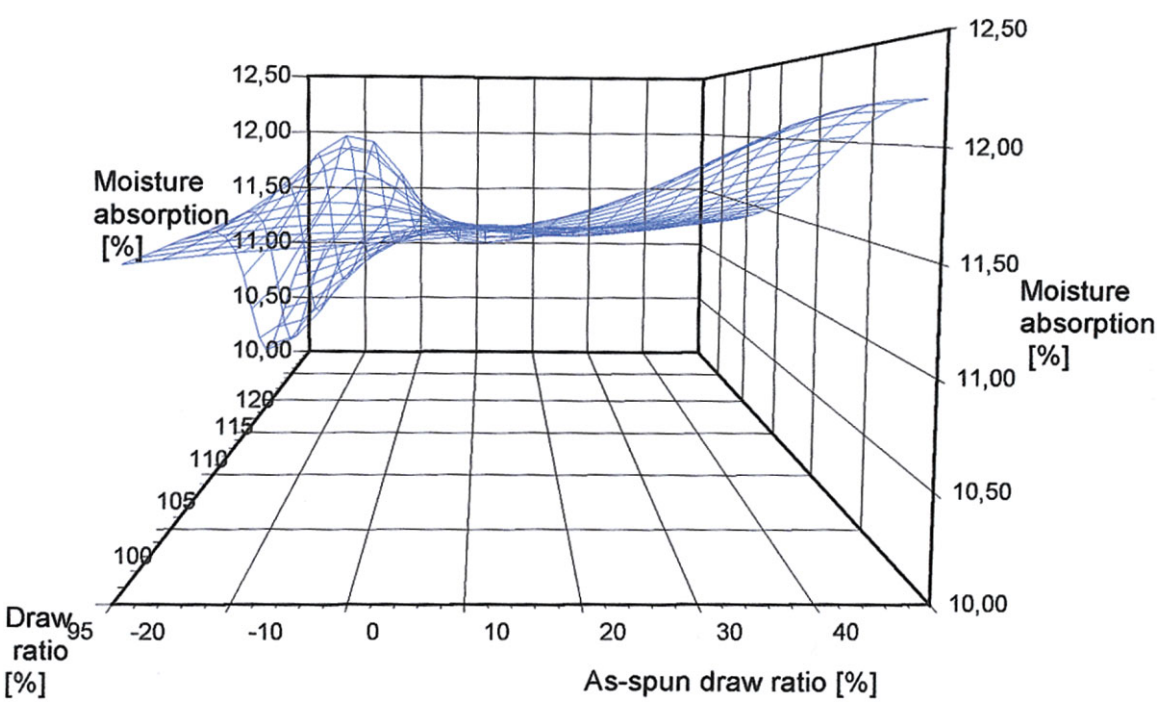

Figure 8 Dependence of moisture absorption at 100% RH on the as-spun draw ratio.

TABLE II
Character of Porous Structure of PIA Nanocomposite Fibers Spun with Varied As-Spun Draw-Out Ratios

		Percentage pore content [%]			
Sample	As-spun draw ratio (%)	Small 4–12.3 (nm)	Medium 15–75 (nm)	Large 150–750 (nm)	Very large 1875–7500 (nm)
M-141/1	50	25.62	43.90	23.18	7.32
M-141/2	25	31.36	40.67	18.64	9.32
M-141/3	10	38.81	43.28	12.69	5.23
M-141/4	−5	21.33	64.93	11.37	2.37
M-141/5	−20	23.92	63.16	9.57	3.36

pore volume (up to 0.75 cm^3/g) and internal surface area (80 m^2/g) as well as with the character of the formed porous structure and the percent content of particular types of pores. For fibers spun with positive values of the as-spun draw-out ratio, the character of the formed porous structure was the same as that of fibers without the nanoadditive.[4]

The curves of pore distribution versus pore radius (Fig. 8) also showed a dimodal character, with a broad maximum comprising the whole range of medium pores. On the other hand, for the fibers from the PIA nanocomposites spun with negative values of the as-spun draw-out ratio, the maxima comprising the whole range of medium-size pores were considerably higher. For the extremely negative values of the as-spun draw-out ratio, an additional high peak appeared at the end of this range. This corresponds to a considerable content of medium pores, ranging from 63% to 65%, resulting in particularly high retention values. For fibers spun in this way, this value ranged from 70% to 73%, whereas for fibers without the nanoadditive spun with a similar as-spun draw-out ratio, retention was lower by almost half. The use of extremely positive values of the as-spun draw-out ratio also enabled PIA nanocomposite fibers with very high retention, above 72%, to be obtained. This was associated with a higher content of large pores, at a level of 23%, with the total content of large and medium pores amounting to 67%. A similar type of porous structure is connected closely with the retention values of fibers without the nanoadditive that were spun with positive values of the as-spun draw-out ratio.

At 100% RH, moisture absorption in the PIA nanocomposite fibers ranging from 11.2% to 12.2% was a result of pores with sizes that allowed moisture absorption by capillary condensation. It can be assumed that they were small- and medium-sized pores from the initial portion of this range. Considering that the total content of both types of pores exceeded even 70%, the structure formed within the whole range of process parameters can be regarded as a fine-porous structure (Table II).

The limited content of very large pores in the formed structure was beneficial in view of the fiber strength. It was lowest, 2%–3%, for fibers spun with negative values of the as-spun draw-out ratio.

From the analysis of the effect of the process parameters under investigation on fiber tenacity and elongation at break (Figs. 9 and 10), it follows that the fibers spun with positive values of the as-spun draw-out

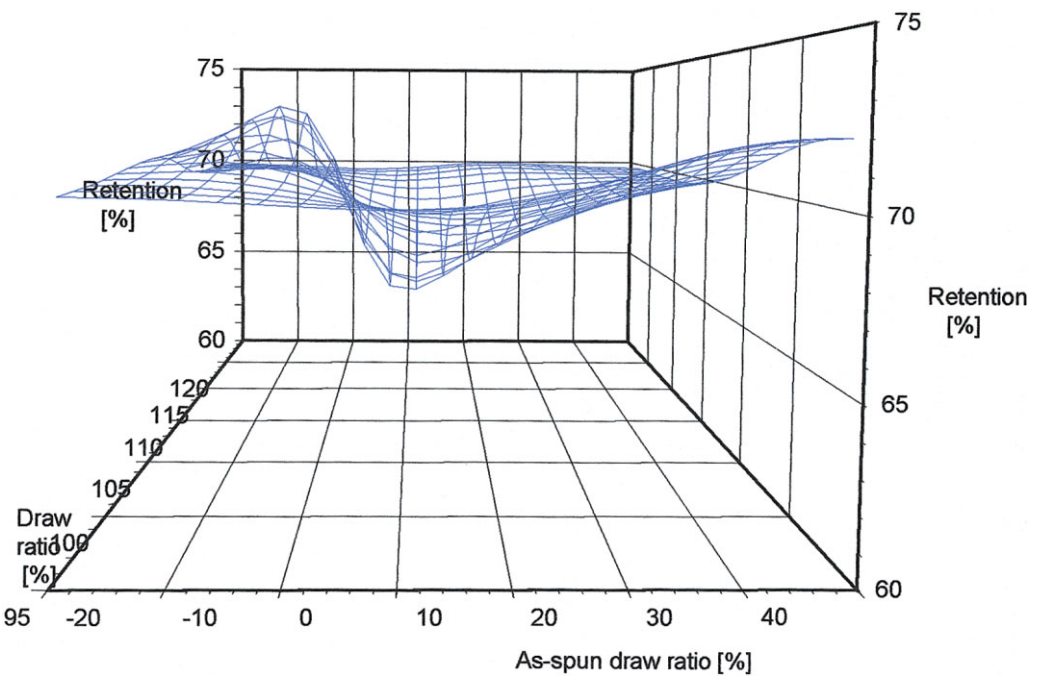

Figure 9 Dependence of retention on the as-spun draw and total draw ratios.

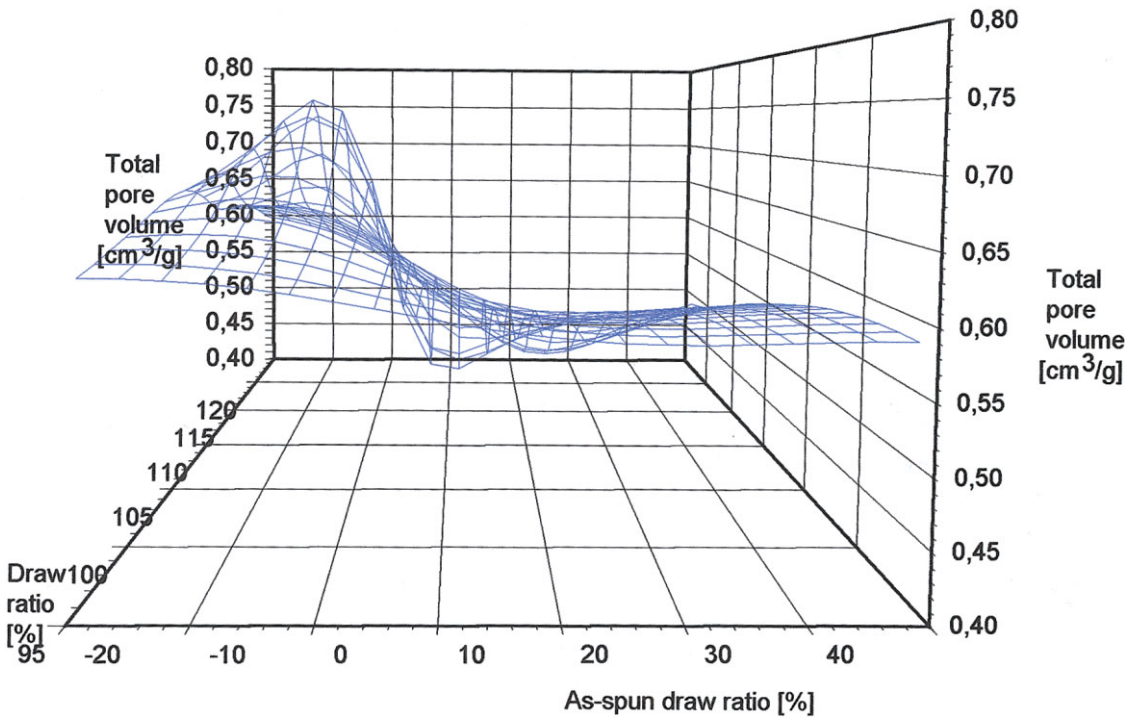

Figure 10 Dependence of total pore volume on the as-spun draw and total draw ratios.

ratio showed higher tenacity, by about 1 cN/tex, than that of fibers spun with negative values of the as-spun draw-out ratio. This was accompanied by an extreme course of changes in this indicator versus the as-spun draw-out and total draw ratios. After exceeding the maximal value corresponding to as-spun draw-out ratios of 20%–30%, tenacity decreased with a decreasing as-spun draw-out ratio. This means that during

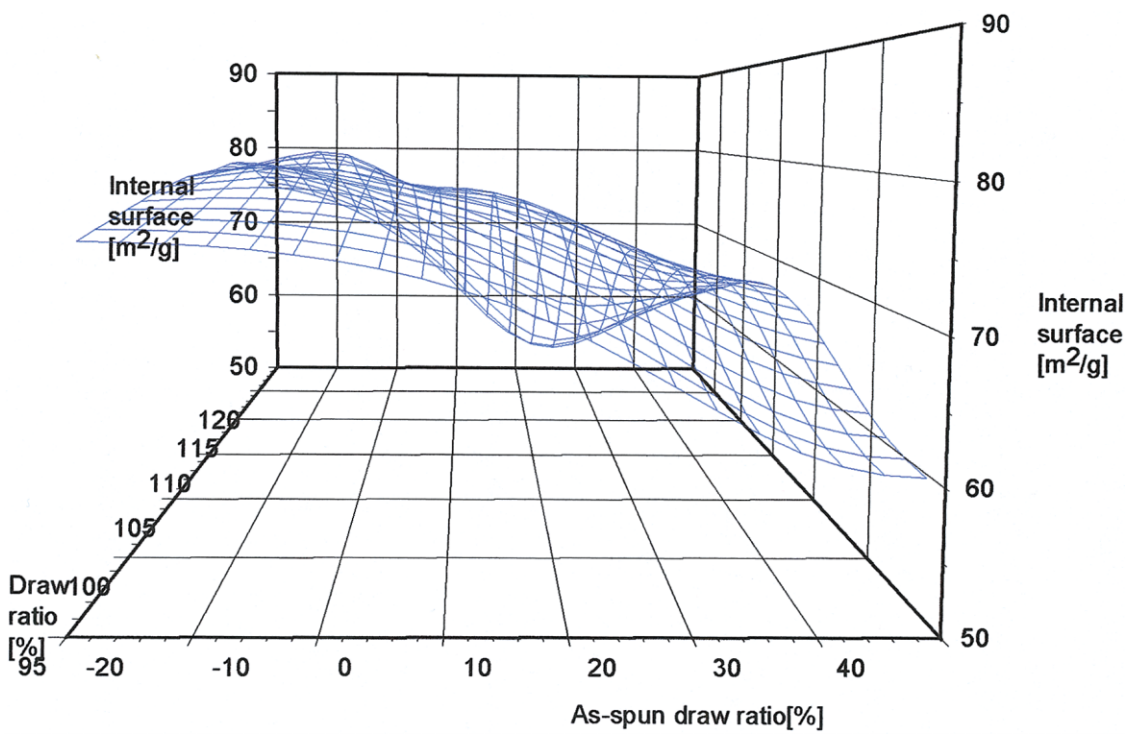

Figure 11 Dependence of the internal surface on the as-spun draw and total draw ratios.

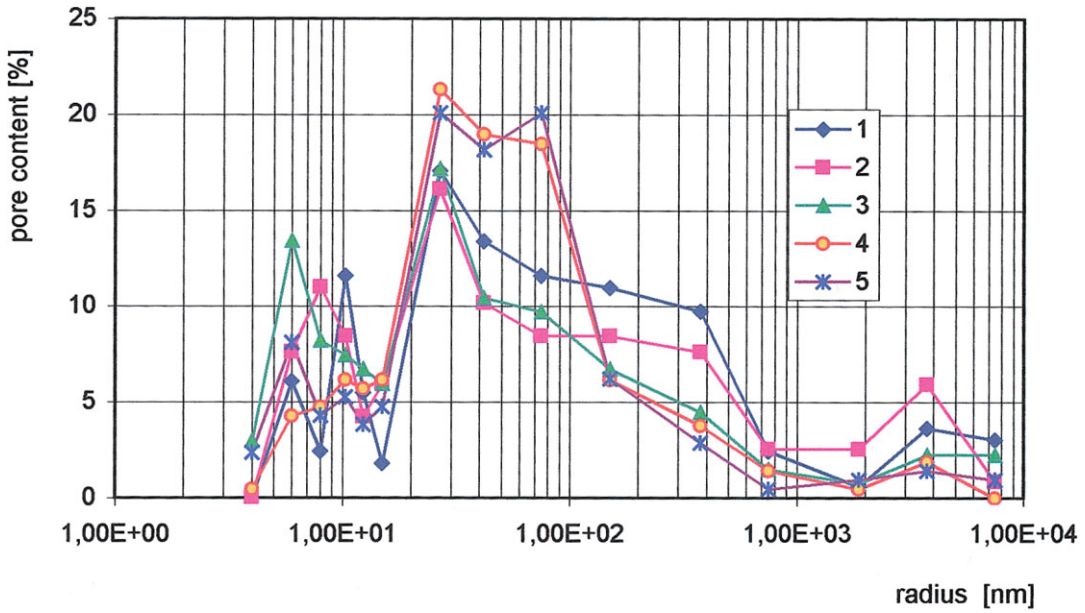

Figure 12 Dependence of pore percentage on pore radius.

fiber spinning from PIA nanocomposites, it was more beneficial to deform the still-fluid stream of solidifying polymer. Under such conditions, the dispersed layers of intercalated MMT in the fiber-forming polymer underwent easier ordering along the axis of the solidifying stream. There also was a better possibility of secondary bonds forming between the amide groups of the macromolecules and the oxygen atoms of the montmorillonite. The use of positive values of the as-spun draw-out ratio also made it possible to obtain higher total deformations. On the other hand, for PIA fibers without MMT, a greater increase in fiber strength was obtained with the use of negative values of the as-spun draw-out ratio. This created more ben-

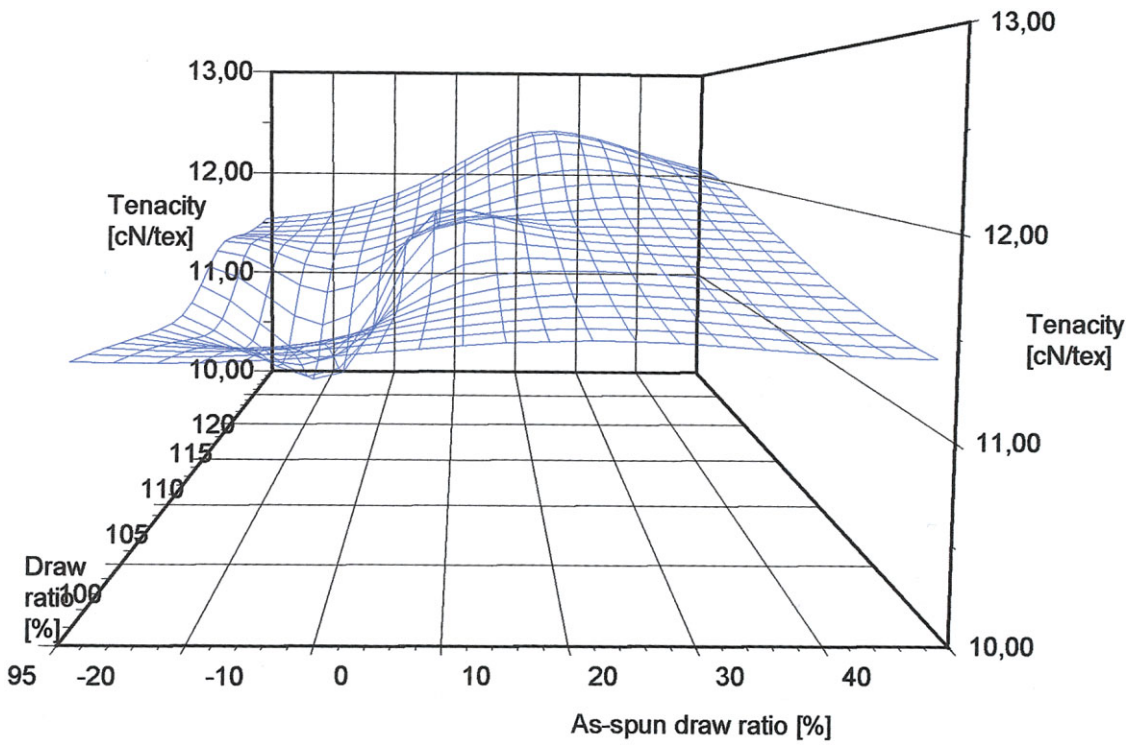

Figure 13 Dependence of fiber tenacity on as-spun draw and total draw ratios.

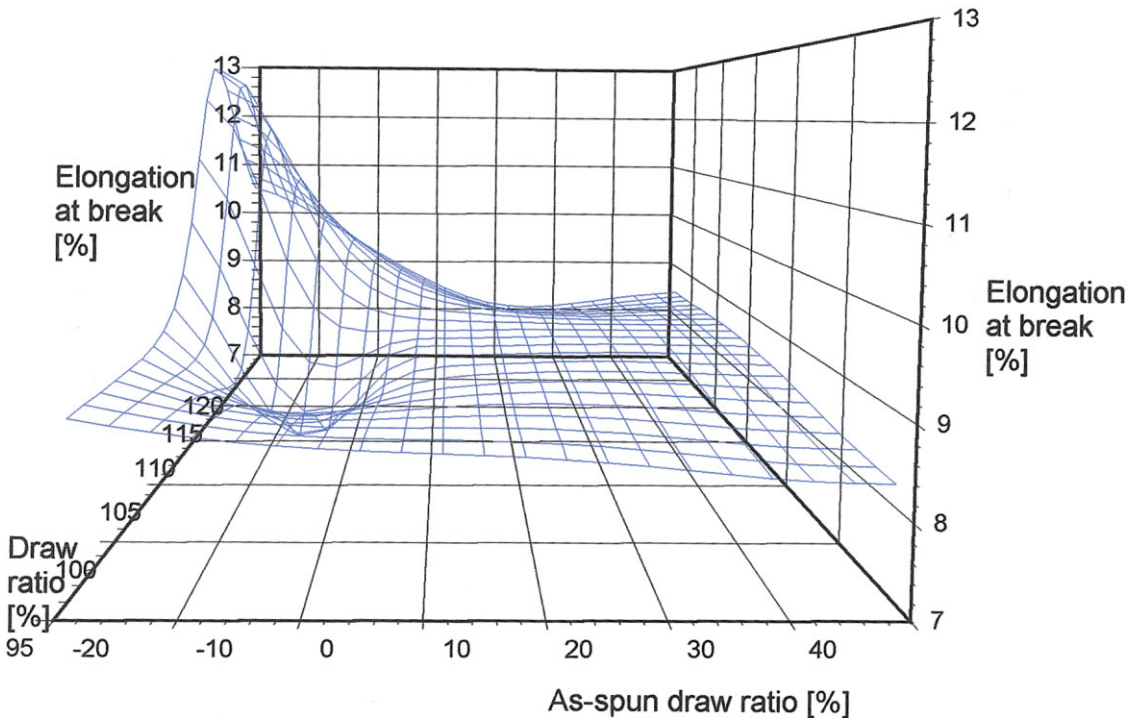

Figure 14 Dependence of fiber elongation at break on the as-spun draw and total draw ratios.

eficial conditions for deformation during the drawing stage and resulted in higher values of the draw ratio.[4] Also, the character of the changes in tenacity was different. A change in the as-spun draw-out ratio toward negative values was accompanied by a considerable increase in the tenacity of fibers from modified PIA. A different course of changes in this parameter occurred for PIA nanocomposite fibers, in accordance with general regularities, which was accompanied by a drop in elongation at break with an increasing as-spun draw-out ratio (Fig. 10). The fibers of the PIA nanocomposites also showed contrasting trends in changes in sorption and strength properties versus the process parameters under investigation. The fibers with the highest strength properties, over 12 cN/tex, were characterized by the lowest total pore volume, but an increased level of 0.42 cm^3/g and an internal surface area of 53.9 m^2/g resulted in good sorption properties. Moisture absorption at 100% RH was 11.1%, and retention was 70%.

Generally, within the whole range of changes in the as-spun draw-out ratio, high sorption properties were obtained for fibers of such a fiber-forming polymer. The magnitude of the increase in total pore volume, reaching 0.75 cm^3/g, and of the increase in the internal surface area, up to 80.68 m^2/g, justifies classifying these fibers as highly porous.

To obtain fibers with high sorption properties and, at the same time, a tenacity suitable for textile processing (over 11 cN/tex), the solidification process has to be carried out under mild conditions in coagulating baths with an increased solvent content, low temperature, and positive values of the as-spun draw-out ratio. Using two values of the as-spun draw-out ratio, 20% or 50%, two types of fibers can be alternately obtained: either fibers with higher tenacity and somewhat lower sorption properties (with an as-spun draw-out ratio of 25%) or with lower tenacity and high sorption properties (with an as-spun draw-out ratio of 50%). The structural pa-

TABLE III
Structural Parameters and Sorption Properties of Fibers Spun under Selected Conditions with Different of As-Spun Draw-Out Ratios

Sample	As-spun draw ratio (%)	Total pore volume (cm^3/g)	Internal surface (m^2/g)	Moisture absorption at 100% RH (%)	Moisture absorption at 100% RH (%)	Retention (%)	Tenacity (cN/tex)	Elongation at break (%)
M-141/2	+25	0.421	53.91	11.12	5.27	70.01	12.15	7.87
M-141/1	+50	0.586	59.75	12.21	5.63	72.00	11.36	8.25

rameters and sorption properties of fibers spun under the selected conditions with different values of the as-spun draw-out ratio are given in Table III.

The magnitude of the improvement in the fiber properties obtained was at a level that will provide high comfort of use of protective clothing made from fibers of this type. At the same time, because of the high heat-resistance properties of fibers from modified PIA,[7] the final fabrics will constitute a barrier to the action of heat flux and flame. An assessment of to what extent the dispersed MMT in polymer will affect the thermal properties of PIA fibers will be the subject of a subsequent publication.

CONCLUSIONS

1. By selecting the conditions for spinning fibers from PIA nanocomposite, multifunctional, highly porous fibers with both high thermal stability (associated with the chemical composition of the polymer) and very good sorption properties can be obtained. The tenacity of these fibers after plasticizing drawing was high enough for textile processing.
2. The incorporation of intercalated montmorillonite into the fiber-forming polymer resulted in a beneficial increase in fiber porosity and internal surface area and, consequently, in increased sorption properties as compared with those of the fibers without the nanoadditive.
3. Fibers from PIA nanocomposites showed similar changes in sorption properties and dissimilar changes in strength properties versus the examined parameters compared to those of fibers from modified PIA.

References

1. Technical information about Kermel fibers of Rhone-Poulenc.
2. Mikołajczyk, T.; Janowska, G.; Urbaniak-Domagała, W.; Szczapińska, M. Fiber Text East Eur 2004, 12, 27.
3. Pigeon, R. Pallard, Die Angewandte. Makromol Chemie 1974, 40, 139.
4. Mikołajczyk, T. Fiber Text East Eur 2002, 10, 52.
5. Mikołajczyk, T.; Skwarski, T. Fiber Text East Eur 2002, 10, 14.
6. Mikołajczyk, T.; Skwarski, T. Fiber Text East Eur 2002, 10, 52.
7. Janowska, G.; Mikołajczyk, T. J Thermal Anal Cal 2003, 71, 549.
8. Kacperski, M. Polimery 2002, 47, 801.
9. Mikołajczyk, T.; Wołowska-Czapnik, D.; Boguń, M. Fiber Text East Eur 2004, 12, 18).
10. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Polym Sci, Part A: Polym Chem 1993, 31, 1755.
11. Mikołajczyk, T. Modyfikacja sposobu wytwarzania włókien poliakrylonitrylowych; Zeszyty naukowe nr 781, Rozprawy naukowe z. 243 Łódź 1997.
12. Mikołajczyk, T.; Szczapińska, M. Rheological Properties of Spinning Solution of a Modified Polyimidoamide Containing Ceramic Nanoparticles; Fiber Text East Eur, to appear.
13. Mikołajczyk, T.; Skwarski T. Fibers Text East Eur 2001, 9, 33.