

Analysis of the Structure and Properties of Polyimidoamide Nanocomposite Fibers Containing Variously Modified Montmorillonite

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ABSTRACT: The effect of fiber-forming conditions on the porous structure, moisture absorption, and strength of polyimidoamide nanocomposite fibers containing montmorillonite modifiers with aminododecane acid has been assessed. It has been found that the final properties of the fibers under consideration depend not only on the parameters of the fiber forming process, but also on the type of modifier used to

change the MMT properties from hydrophilic to organophilic. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1103–1108, 2006

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

INTRODUCTION

The use of nanocomposites as fiber-forming polymers makes it possible to produce fibers with increased functionality and new features, incomparable with those of conventional synthetic fibers.

Owing to the chemical structure of their fiber-forming polymers, polyimidoamide (PIA) fibers show a high thermal resistance, predisposing them to be used as the so-called first-contact-with-flame materials. On the other hand, their good thermoinsulating properties are utilized in technical applications.

Heat-resistant PIA fibers with increased porosity and moisture absorption, and with tenacity being suitable for textile processing,^{1,2,3} have been obtained by modification of the fiber-forming polymer and proper selection of fiber-spinning conditions. At the same time, these fibers have retained their high thermal stability.⁴ These features are of great importance for protective clothing, as they provide an enhanced comfort for its use. However, the increased fiber porosity may result in some decrease in the protective properties of clothing against flame.

The incorporation of nanomontmorillonite into modified PIA compensates this disadvantageous effect of increasing the porosity, and the PIA nanocomposite fibers obtained are characterized by an in-

creased barrier effect to the action of heat and flame when compared with fibers without nanoadditives.⁵

The montmorillonite (MMT) packages coated with a thin layer of carbonized polymer on their surface, and dispersed in the fiber-forming polymer matter constitute a barrier which cuts off oxygen access and consequently prevents flame propagation.⁵ At the same time, the laminar structure of MMT and the strongly developed interface surface provide an increased porosity and moisture absorption to the fibers.⁶

The effect obtained is connected with the supermolecular and morphological structure of fibers, being dependent on the fiber-spinning conditions, as well as on MMT, characterized by a specific laminar structure,⁷ which is incorporated into the fiber-forming matter.

The character of interactions between the laminar MMT and the polymer matrix has been explained in detail, by taking PA6 as an example. The authors explain the improvement in tensile properties of such a nanocomposite by the occurrence of secondary bonds between the oxygen atoms of MMT and the amide groups of polymer macromolecules.⁸

Considering the presence of such strong interactions between the polymer and the laminar MMT nanoadditive, the properties of the nanocomposite fibers can also be affected by the chemical composition of the modifier used to change the hydrophilic properties into organophilic. Such influence is possible because interactions may occur between the functional groups of alkylammonia compounds used to modify MMT and the polymer under discussion. The properties of nanocomposites depend, to a considerable extent, also

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TABLE I
Characteristics of the Spinning Solution of PIA
containing MMT in *N*-methylpyrrolidone

Symbol of solution	M-142
Concentration (%)	19.78
Intrinsic viscosity η (dL/g)	1.63
Apparent dynamic viscosity (Pa s)	30.95
Rheological parameters	
n	0.9948
k	29.576

on the length of the aliphatic chains of amino acids or their ammonia salts used for MMT modification. It has been also found that longer chains of these compounds facilitate the intercalation process.⁹

The aim of this study was to assess the effect of fiber-forming conditions on the porous structure, the sorption, and strength properties of PIA nanocomposite fibers containing MMT modified with aminododecane acid. It was also intended to evaluate the effect of MMT dispersed in the polymer and the type of modifier used for its intercalation.

Considerations concerned with the investigation of properties of fibers from PIA nanocomposite including MMT modified by an amine of long aliphatic chains will be the subject of a subsequent publication.

EXPERIMENTAL

MMT modified with aminododecane acid was added to the postreaction PIA solution in the form of a suspension in *N*-methylpyrrolidone under conditions described in Ref. 10.

The modification of sodium MMT from Nanocor with aminododecane acid was carried out according to the method developed by the Committee of Scientific Research (funded by the Project No. 4T08E078724). It was performed at the Institute of Industrial Chemistry, Warsaw, under the supervision of Dr. M. Kędzierski.

As a result of this modification, the interlayer distances of MMT were increased from 1.33 nm for sodium MMT to 1.99 nm for the modified MMT. These values were calculated on the basis of the position of the first low-angle diffraction maximum. After disintegration, the grain sizes were in the range from 2 to 20 μm .

The elementary analysis of carbon, hydrogen, and nitrogen for MMT modified by aminododecane acid was carried out with the use of PE Series II CHNS/ON analyzer from Perkin-Elmer. The following results were obtained: 17.81% (16.31%) of Carbon, 2.98% (2.96%) of Hydrogen, and 1.71% (1.59%) of Nitrogen. The values in brackets are theoretical values related to the total exchange of MMT cations. This means that the elementary analysis indicates a carbon content that

is increased by 9% in relation to the ion-exchange efficiency of 100%. A similar result (7.5%) was stated for the analysis of nitrogen. From these results, it appears that MMT modified by aminododecane acid contains some amount of free ammonium compound besides organic cations that are ion bound.

The characteristics of spinning solutions are given in Table I. Moisture absorption at 65 and 100% of relative air humidity was determined by the desiccative method, in accordance with Polish Standard PN-71/P-04635.

Water retention was measured by the method 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/s^2 .

Fiber tenacity and elongation at break were measured in accordance with Polish Standard PN-85/P-04761/04, 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 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.⁴

Fibers were spun from the polymer solution by the wet-spinning process by 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 tem-

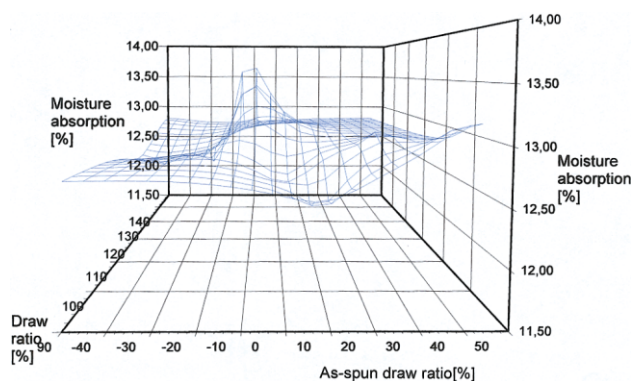


Figure 1 Dependence of moisture absorption at 100% RH on the as-spun draw ratio. [Color figure can be viewed in the online issue, which is available at <http://www.interscience.wiley.com>.]

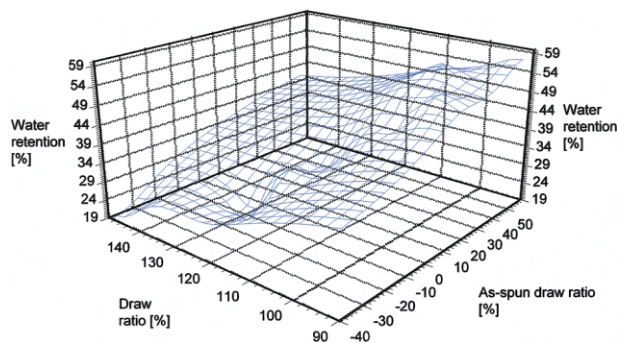


Figure 2 Dependence of retention on the as-spun draw ratio and total draw ratio. [Color figure can be viewed in the online issue, which is available at <http://www.interscience.wiley.com>.]

perature of about 15–18°C. The drawing process was performed in a single stage, in a plasticizing bath containing the same amount 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.

RESULTS AND DISCUSSION

By using the process of fiber forming from solution, the properties of fibers depend on the structure obtained during the solidification stage. According to the diffusion or the drop mechanism, the proceeding of solidification influences the formation of a structure with defined porosity and susceptibility to deformation during the drawing stage. To obtain the fine-porous structure that is characteristic of the diffusion mechanism, the solidification process was carried out under mild conditions in a coagulation bath containing 55% of solvent at a low temperature of 15°C. Such conditions were also suitable for the formation of fibers with increased strength, which depend on the

value of the as-spun draw ratio and the related deformation during fiber drawing. The as-spun draw ratio was changed within a wide range from positive to negative values, i.e., from 53% to –39%.

From the analysis of sorption properties, it follows that both the moisture absorption at 100% RH (Fig. 1) and the water retention (Fig. 2) show an upward trend with increasing in the as-spun draw ratio (Table II). Within the range of positive values of the as-spun draw ratio, it is possible to obtain higher (by about 2%) values of moisture absorption at 100% RH and retention values higher by as much as 20% as compared with the values obtained for fibers spun with negative as-spun draw ratios. The moisture absorption at 65% RH changes, versus the process parameters, just within 1%. Its value is higher by about 1.5% than that of PIA nanocomposite fibers containing MMT (Nanomer PGW) in addition to their chemical structure. It is due to the fact that MMT was modified with aminododecane acid. The presence of acid groups in the polymer and the considerably higher contents of small pores (capable of absorbing moisture through capillary condensation) also seem to be the cause of higher (by 1–1.5%) moisture absorption at 100% RH of the fibers containing MMT modified with aminododecane acid.

The curves of pore distribution versus pore radius, with the pore distribution showing bimodal character, are characterized by high maximum within the range of small pores almost twice as as that of fibers containing MMT (Nanomer PGW) (Fig. 3). On the other hand, the lower maximum within the range of medium pores is consistent with lower retention values by about 20% of the fibers containing MMT modified with aminododecane acid, spun at positive values of the as-spun draw ratio. For fibers spun at negative values of this parameter, the retention value is lower even by 50% as the retention value which depends on the pores that are large enough to allow water pene-

TABLE II
Structural Parameters and Properties of Fibers from PIA Nanocomposite

Symbol of sample	As-spun draw 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)	Elongation (%)
M 142/10	–39.3	148.2	0.195	26.704	7.77	12.81	20.11	15.11	15.92
M 142/9	–30.9	122.9	0.147	23.895	7.74	12.41	27.03	14.28	16.38
M 142/8	–19.64	123.1	0.210	35.438	6.98	12.47	22.78	13.62	13.75
M142/7	–10.9	115.6	—	—	7.47	12.52	36.31	12.82	12.41
M 142/6	0	116.1	0.192	26.883	7.66	13.70	33.09	12.36	11.18
M 142/5	+10.25	102.7	—	—	7.35	12.51	45.03	11.88	11.39
M 142/4	+18.2	95.4	0.416	55.418	7.30	12.40	54.53	10.41	11.23
M 142/3	+26.2	103.1	0.366	55.385	6.93	12.83	53.31	10.51	9.66
M 142/2	+34.8	102.0	0.473	65.206	6.95	13.01	57.97	10.59	8.93
M 142/1	+53.1	90.1	0.508	65.054	6.93	13.18	58.59	10.21	8.14

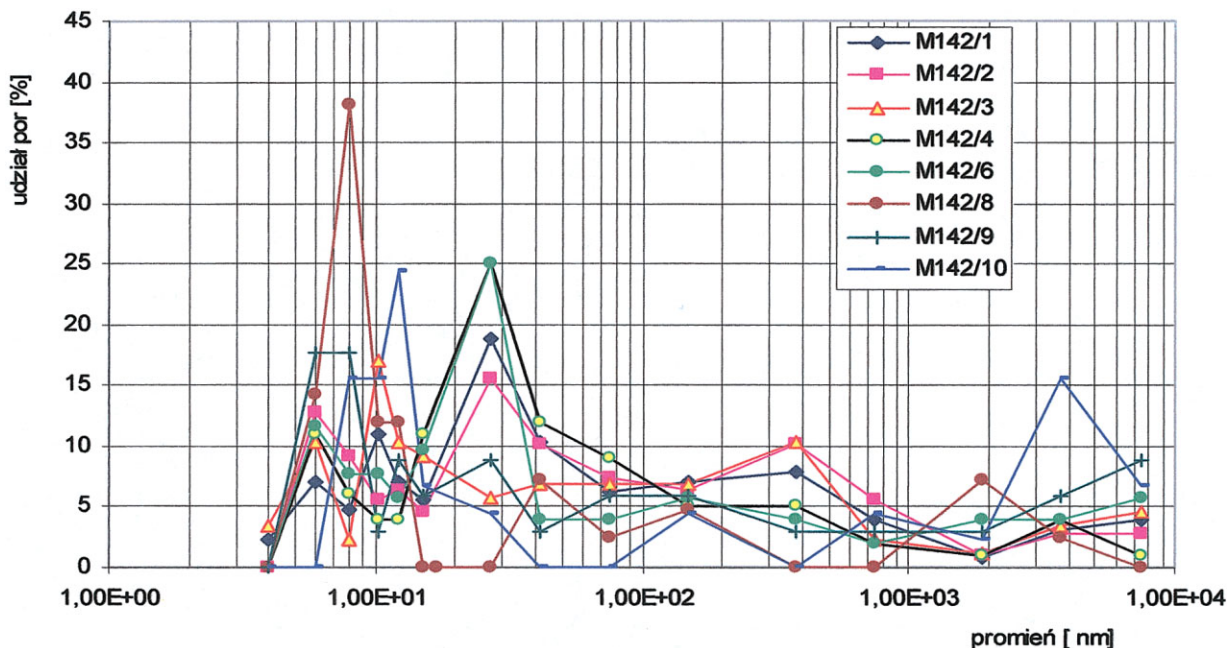


Figure 3 Dependence of pore percentage on pore radius. [Color figure can be viewed in the online issue, which is available at <http://www.interscience.wiley.com>.]

tration, and at the same time small enough to retain water during its mechanical removal.

With comparable contents of large pores (Table III), the fibers of PIA nanocomposite containing Nanomer PGW are characterized by higher, even by 50%, number of medium pores, especially those from the upper part of this range.⁶ According to our findings,¹¹ the pores with such dimensions determine the retention value. Therefore, it is clear that fibers with such a porous structure show higher values of retention. The character of changes in sorption properties of PIA nanocomposite fibers is consistent with the increase in the total pore volume (Fig. 4) and the internal surface (Fig. 5) with increase in the as-spun draw ratio (Table

II). Both these structural parameters of fibers containing MMT modified with aminododecane acid assume lower values, namely 0.2–0.5 cm³/g and 24–65 m²/g, respectively, than those of fibers containing Nanomer PGW whose total pore volume ranges from 0.4 to 0.7 cm³/g and internal surface from 55.3 to 80.6 cm²/g. At the same time, Nanomer PGW-containing fibers show lower moisture absorption at 100% RH and a higher retention than those of PIA nanocomposite fibers containing MMT modified with aminododecane acid. This confirms the fact found by us on frequent occasions, that the sorption properties of fibers depend not only on the total pore volume and internal surface, but also on the characteristic of the created porous structure.

TABLE III
Character of the Porous Structure of PIA Nanocomposite Fibers Spun with Variable Values of As-Spun Draw Out Ratio

Sample	As-spun draw ratio (%)	Percentage pore content (%)			
		Small [4–12.3] (nm)	Medium [15–75] (nm)	Large [150–750] (nm)	Very large [1875–7500] (nm)
M 142/10	−39.3	55.56	11.11	8.88	24.45
M 142/9	−30.9	47.06	23.52	11.76	17.64
M 142/8	−19.6	64.29	19.04	7.14	9.52
M 142/7	−10.9	—	—	—	—
M 142/6	0	32.69	42.32	11.54	13.47
M 142/5	+10.25	—	—	—	—
M 142/4	+18.2	25.00	57.00	12.00	6.00
M 142/3	+26.2	43.19	28.41	19.32	9.10
M 142/2	+34.8	33.93	37.62	22.01	6.42
M 142/1	+53.1	32.28	40.95	18.90	7.88

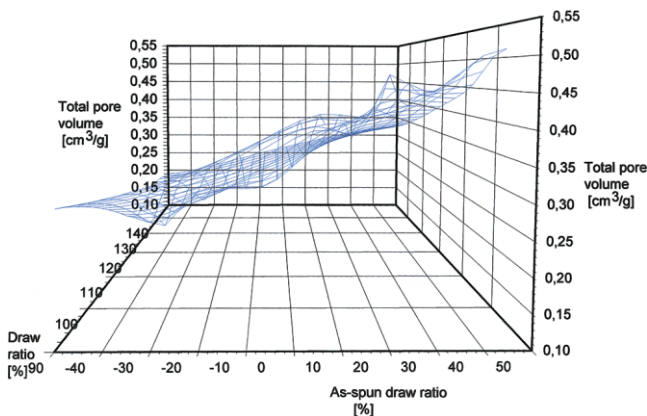


Figure 4 Dependence of total pore volume on the as-spun draw ratio and total draw ratio. [Color figure can be viewed in the online issue, which is available at <http://www.interscience.wiley.com>.]

A change in the as-spun draw ratio towards negative values results in increased tenacity (Fig. 6) and elongation at break (Fig. 7) of PIA nanocomposite fibers (Table II). The fibers spun with an extremely negative value of as-spun draw ratio show a tenacity of 15.1 cN/tex, whereas the tenacity of fibers spun with an extremely positive value of as-spun draw ratio is lower by about 5 cN/tex. On the other hand, in the case of fibers containing Nanomer PGW, it has been found that it is beneficial to form the fibers with positive values of as-spun draw ratio at a level of 20% because of the strength properties of the PIA nanocomposite fibers obtained. At the same time, the changes in tenacity as a function of as-spun draw ratio and deformation during drawing show a course with maximum.⁶

Thus, one may assume that the characteristic of the relationships obtained as well as the fiber tenac-

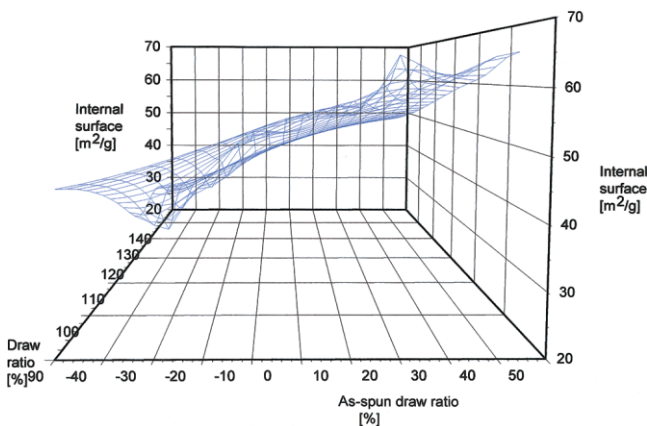


Figure 5 Dependence of internal surface on the as-spun draw ratio and total draw ratio. [Color figure can be viewed in the online issue, which is available at <http://www.interscience.wiley.com>.]

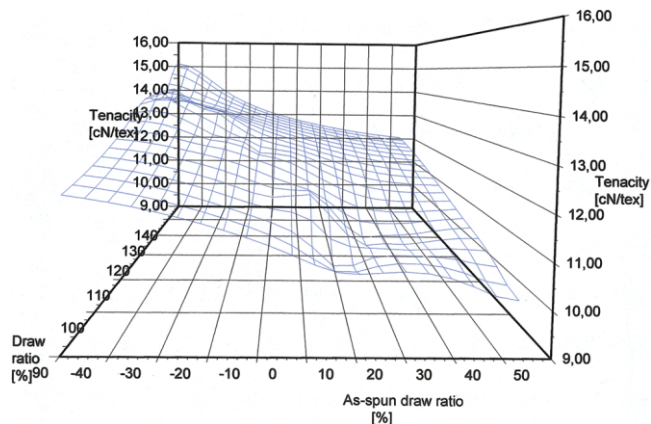


Figure 6 Dependence of fiber tenacity on the as-spun draw ratio and total draw ratio. [Color figure can be viewed in the online issue, which is available at <http://www.interscience.wiley.com>.]

ity is affected to some extent by the type of the compound used to modify MMT. In the case of using aminododecane acid, additional secondary bonds can be formed with the amide groups of polymer. The increase in the number of secondary bonds in comparison with Nanomer PGW-containing PIA fibers, where only bonds between amide groups and the oxygen atom of MMT layers occur, results in higher fiber tenacity. The different characteristic of the relationship between tenacity and the as-spun draw ratio and the total draw ratio for fibers containing both kinds of MMT used can be probably explained as follows. It is known that fiber strength properties depend on the orientation of structural elements (also including MMT layers), the quantity, and the density of secondary bonds between macromolecules of the polymer and those between the later and the dispersed layers of inter-

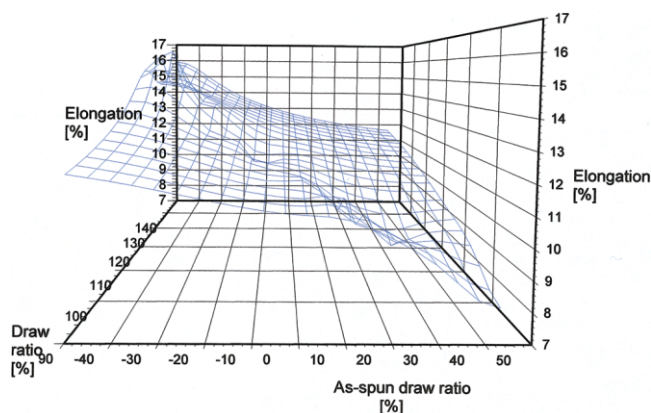


Figure 7 Dependence of fiber elongation at break on the as-spun draw ratio and total draw ratio. [Color figure can be viewed in the online issue, which is available at <http://www.interscience.wiley.com>.]

calated or exfoliated MMT. A significant effect on the fiber strength is also exerted by the structural defects of fibers, and, in addition to the total pore volume, the presence of very large pores. Their size and quantity can be directly connected with the size of MMT packages and their agglomeration. One may assume that in the case of fibers containing Nanomer PGW, it is the orientation of MMT layers in the still liquid stream that determines the changes in fiber strength. Therefore, higher strength values can be obtained for fibers spun with positive values of as-spun draw ratio. On the other hand, in the case of fibers containing MMT modified with aminododecane acid, the fiber tenacity depends on the number of secondary bonds, while the characteristic of the relationship obtained is the same as that for PIA without the nanoadditive.¹ Also the order of magnitude of the strength is similar (about 15 cN/tex). The lower tenacity (maximum up to 12 cN/tex) of fibers containing Nanomer PGW may be connected also with the formation of larger MMT agglomerates. This can increase the porosity up to 0.7 cm³/g, but it can also decrease the tenacity of the fibers containing Nanomer PGW. Such an interpretation is confirmed by the fact that an increased content of MMT modified with aminododecane acid in the polymer (up to 5% of the polymer weight) causes no significant changes in the fiber tenacity. The decrease in the ability to deform, connected with the incorporation of a higher quantity of nonfiber-forming nanoadditive, has been compensated by the formation of additional secondary bonds between polymer macromolecules and MMT layers and aminododecane acid used for its modification. The tenacity of fibers spun with a negative as-spun draw ratio of -20% amounts in this case to 13.5 cN/tex, being of the same order of magnitude as that for fibers containing 3% of MMT.

CONCLUSIONS

1. The structure and properties of PIA nanocomposite fibers depend on the fiber-forming parameters, the presence of MMT nanoadditive in the polymer, and on the type of the modifier used to change the MMT properties from hydrophilic to organophilic.
2. The change in the characteristic of the fiber porous structure is connected with the incorporation of MMT modified with aminododecane acid into the fiber-forming polymer. With a lower total pore volume and internal surface, this results in lower moisture absorption at 100% RH and almost twice as low retention as that of fibers containing PGW Nanomer.
3. The incorporation of MMT modified with aminododecane acid into the polymer causes the fiber tenacity to increase by about 3 cN/tex as compared with that of PGW Nanomer-containing fibers. This seems to be associated with the formation of additional secondary bonds between the polymer macromolecules and the modifier used.

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