Effect of Fiber-Forming Conditions and Type of MMT Modifier on the Structure and Properties of Multifunctional Polyimideamides Nanocomposite Fibers

Teresa Mikołajczyk, Magdalena Olejnik

Department of Man-Made Fibers, Faculty of Textile Engineering and Marketing, Technical University of Łódź, 90924 Łódź, Poland

Received 10 March 2006; accepted 12 July 2006
DOI 10.1002/app.25314
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of fiber-spinning conditions on the structure, sorption, and strength properties of polyimideamides (PIA) nanocomposite fibers has been examined. Montmorillonite (MMT) modified with octadecylamine was used as a nanoadditive. The properties of fibers containing differently modified MMT were compared. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2940–2944, 2007

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

INTRODUCTION

The use of montmorillonite (MMT)-containing polyimideamides (PIA) nanocomposite as fiber-forming polymer makes it possible to produce thermo-resistant fibers with enhanced functionality and increased protection against the action of heat and flame.

The modification of fiber-forming polymer by incorporating into the macromolecular chain flexible segments derived from diaminediphenylmethane, as well as a proper selection of fiber-forming conditions, have resulted in obtaining of fibers with increased moisture absorption and a strength at a level of 15 cN/tex.[1–3] Their high thermal stability remained unchanged.[4]

High sorption properties as for a hydrophobic polymer, ensuring an increased comfort of use for protective clothing, are connected with increased fiber porosity, in turn adversely affecting fiber inflammability.

The incorporation of disperse MMT into the fiber-forming polymer made it possible to obtain PIA nanocomposite fibers with good sorption properties, reduced flammability, but with a tenacity at a level of 12 cN/tex.[5] The strength properties of fibers depend on the susceptibility of their structure to deformation during the drawing stage. The presence of a non-fiber-forming nanoadditive decreases this susceptibility. Besides the parallel arrangement of the MMT layers along the fiber axis, the type of MMT dispersion in the fiber-forming polymer (intercalation or exfoliation) exerts a significant influence on the level of strength properties. As we have reported,[6] lower strength properties of PIA fibers containing MMT (Nanomer PGW) compared with those of PIA fibers without the nanoadditive appear to be due to the subsidence of MMT galleries with the lack of complete exfoliation of MMT. The type of modifier used to change the hydrophilic properties of MMT to hydrophobic may also influence this effect.

The use of aminododecane acid as a modifier makes it possible to create additional secondary bonds between the polymer macromolecule and acid groups of the modifier.[7] No such possibility exists when MMT is modified with octadecylamine, which can have a bearing on the level of obtained strength properties.

In contrast, the sorption properties of fibers (i.e., moisture absorption at 100% RH, water retention) are connected with the total pore volume and the character of created porous structure.[6,7] These parameters are also affected by the formation of MMT agglomerates. Their bonds with the polymer matrix are weaker than those of the intercalated laminar systems, in which the chains of polymer macromolecules penetrate inside the inter-layer galleries. The presence of these agglomerates causes an increase in the porosity of PIA nanocomposite fibers containing Nanomer PGW.[5]

Both the character of changes and the level of structural parameters, sorption, and strength properties are affected not only by the process parameters of fiber formation, but also by the type of MMT modifier. We have confirmed this, using aminododecane acid as a modifier.[7]

Correspondence to: T. Mikołajczyk (mikolter@mail.p.lodz.pl).
Contract grant sponsor: Polish State Committee for Scientific Research; contract grant number: 3T08E01029; 4T08E08724.

Journal of Applied Polymer Science, Vol. 103, 2940–2944 (2007)

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

Symbol of solution	Conc (%)	Intrinsic viscosity (η) (dcl/g)	Apparent dynamic viscosity (Pas)	Rheological parameters	
				n	k
M-149	20.04	1.53	20.02	0.98	23.75

The aim of the present study is to assess the effect of fiber-forming conditions on the structure and properties of PIA nanocomposite fibers containing MMT modified with octadecylamine. Their properties will be compared with those of PIA nanocomposite fibers containing MMT modified with aminododecane acid, also taking into consideration the effect of MMT agglomerate breaking by means of ultrasound.

MATERIALS AND METHODS

MMT modified with octadecylamine was added to the postreaction PIA solution in the form of a suspension in *N*-methylpyrolidone under conditions we have described previously.[8]

The modification of sodium MMT from Nanocor with octadecylamine was carried out according to the method developed by the Committee of Scientific Research (funded by Project 4T08E078724), performed at the Institute of Industrial Chemistry, Warsaw, under the supervision of Dr. M. Kędzierski.

As a result of this modification, the inter-layer distances of MMT were increased from 1.33 nm for sodium MMT to 3.12 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 within the range of 2–20 μm.

The elementary analysis of carbon, hydrogen, and nitrogen for MMT modified with octadecylamine was carried out with the use of the PE Series II CHNS/ON analyzer from Perkin-Elmer (Wellesley, MA). The following results were obtained: 31.72% (23.03%) of C, 5.31% (4.19%) of H, and 2.05% (1.49%) of N. 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 increased by 38% in relation to the ion exchange efficiency of 100%. A similar result (+38%) was stated for the analysis of nitrogen. It results from this appears that MMT modified by octadecylamine contains some amount of free ammonium compound besides organic cations ion-bounded.

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-80/P-04635.

Water retention was measured using a centrifuge. Fiber samples were immersed in distilled water containing a surface-active agent (Rokafenol Nx-3 in the amount of 0.1%) for 24 h; 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-EN-ISO-2062 : 1997, referring the breaking force to the fiber linear density in tex.

Fiber porosity was measured by means of a Carlo-Erba mercury porosimeter, linked to a computer system to register the numerical values of the parameters measured. The values measured included total pore volume, total internal surface, volume of the capillary group with a defined radius, and percentage content pores. This method allows us to determine the pore percentage content within the given ranges in the total capillary size range of 5–7500 nm.[9]

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 with continuous control. Spinnerets with 240 orifices of 0.08-mm diameter were used. The solidification process was carried out in a bath containing an aqueous solution of the solvent (>55%) at a low temperature (~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.

RESULTS AND DISCUSSION

Similarly to our previous studies on the preparation of PIA nanocomposite fibers containing Nanomer PGW or MMT modified with aminododecane acid,[5,7] the process of fiber solidification was carried out in mild coagulation baths (NMP content 55%) at low temperatures (15–18°C). In this way, the conditions were made appropriate to carry out the fiber solidification according to the diffusive mechanism and to create a fine porous structure being beneficial for the strength properties of fibers. The as-spun draw-out ratio was changed within a wide range from negative

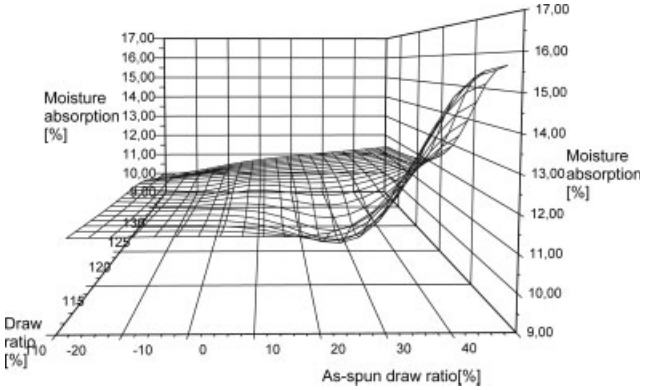

Figure 1 Dependence of moisture absorption at 100% RH on the as-spun draw ratio.

(−20%) to positive (+50%) values. The extent of deformation during the plasticizing drawing stage was variable and was dependent on the as-spun draw-out ratio. Because of the increased molecular mobility of polymer macromolecules, this process stage was carried out in a plasticizing bath with solvent (NMP) content similar to that of the solidification bath at elevated temperature (60–70°C) to create beneficial conditions for fiber deformation. As was previously found (by the Polish State Committee for Scientific Research), the effectiveness of drawing fibers from polymer with a rigid structure of macromolecules depend largely on the extent of draw ratio, while the value of tensile stress is of lesser importance.

It follows from the analysis of sorption properties (Figs. 1 and 2) that the character of changes in moisture absorption and water retention versus variable process parameters is similar to that observed previously for PIA nanocomposite fibers containing Nanomer PGW and MMT modified with aminododecane acid. The moisture absorption at 100% RH shows a clear upward trend with increasing as-spun draw-out ratio, assuming the highest values of 15.5% for fibers formed with the extremely positive value of as-spun draw-out ratio. The moisture absorption at

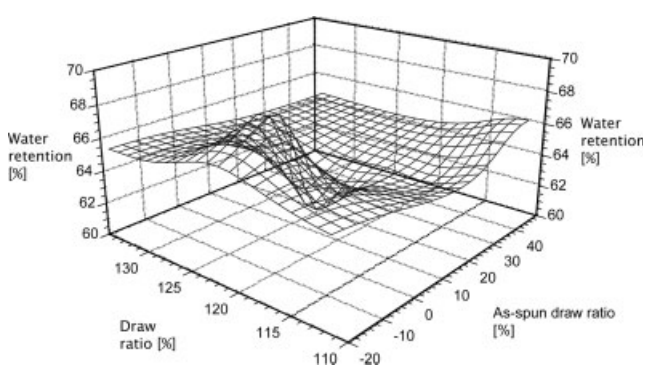

Figure 2 Dependence of retention on the as-spun draw ratio and total draw ratio.

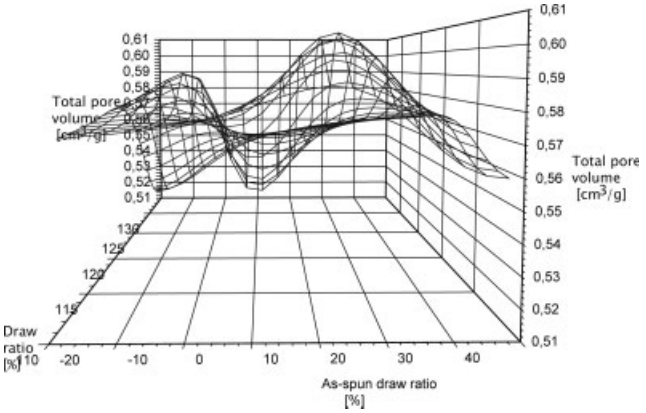

Figure 3 Dependence of total pore volume on the as-spun draw ratio and total draw ratio.

65% RH ranges slightly from 4.1% to 4.4%, assuming the lowest values in comparison with other PIA nanocomposite fibers. It is clear that this parameter is connected mainly with the chemical composition of the fiber-forming polymer. The presence of acid groups in MMT modified with amninododecane acid makes it possible to chemically combine water, which explains the high values (over 7%) of moisture absorption at 65% RH of fibers containing a nanoadditive modified in this way.[7]

The value of water retention (Fig. 2) shows an upward trend within the range of positive values of as-spun draw-out ratio, but the highest value of this parameter 68.5% is shown by the fibers spun with a negative value of as-spun draw-out ratio of −5%. These values are higher by about 10% in comparison with the maximum values obtained for PIA fibers containing MMT modified with aminododecane acid. This is consistent with the values of the total pore volume (Fig. 3) and internal surface (Fig. 4), which are 0.61 cm^3/g and 75.8 m^2/g, respectively, for PIA fibers containing MMT modified with octadecylamine. The values of these

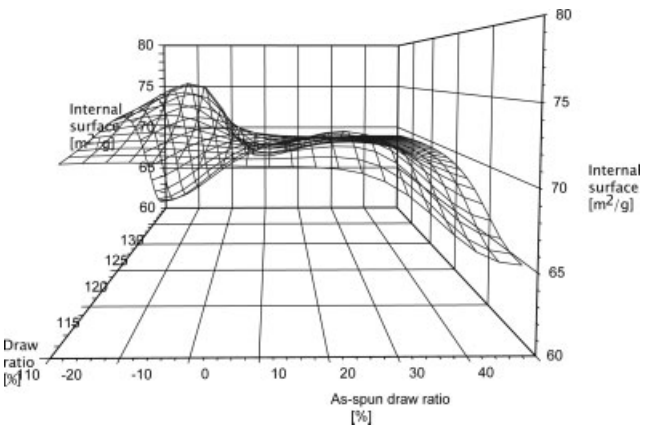

Figure 4 Dependence of internal surface on the as-spun draw ratio and total draw ratio.

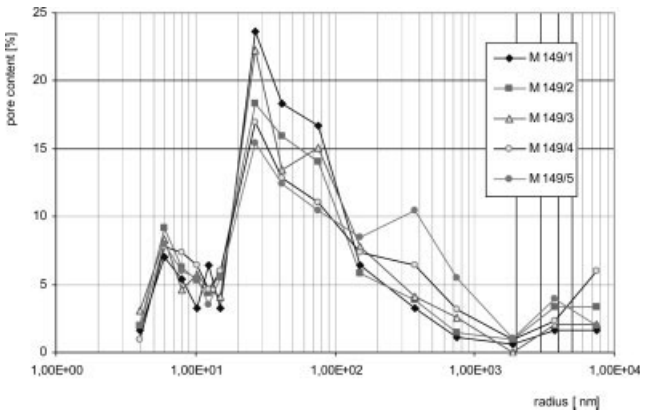

Figure 5 Dependence of pore percentage on pore radius.

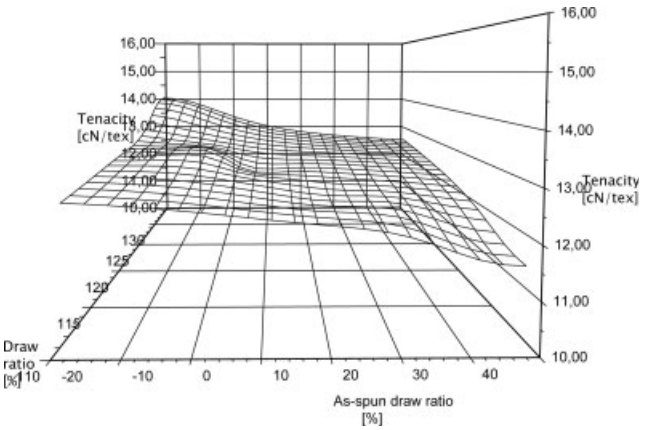

Figure 6 Dependence of fiber tenacity on the as-spun draw ratio and total draw ratio.

parameters entitle one to classify the PIA nanocomposite fibers to fibers with increased porosity. The total pore volume (Fig. 3) as a function of variable process parameters shows a general upward trend except for the values for the extremely positive as-spun draw-out ratio. The highest values of total pore volume and internal surface amounting to 0.59 and 0.6 cm^3/g and 75.86 and 72.41 cm^2/g, respectively are shown by fibers spun with negative value of as-spun draw-out ratio at a level of −5% and with its positive value of +25%. At the same time, the dependence of internal surface to as-spun draw-out ratio and total draw ratio shows a downward trend (Fig. 4) with increasing of the as-spun draw-out ratio similarly as in the case of PIA nanocomposite fibers containing Nanomer PGW.[5] In contrast, in the case of fibers containing MMT modified with aminododecane acid, both the total pore volume and internal surface show clearly upward trend with increasing the as-spun draw-out ratio.[7] Thus, one may believe that both structural parameters are affected not only by the fiber-forming conditions, but also by the type of modifier used to change the properties of MMT from hydrophilic to hydrophobic.[10]

All the types of PIA nanocomposite fibers show similar characteristics in the distribution of pores as a function of their radius. The curves of pore distribution (Fig. 5) of fibers spun with various values of as-spun draw-out ratio show a bimodal character with a high characteristic maximum within the range of medium size pores. The presence of such pores, whose size is large enough to make them capable of absorbing the water and at the same time small enough to hold water during its mechanical removal, causes the water retention to increase.[9] Fibers spun with the extremely negative as-spun draw-out ratio, despite the highest maximum within the range of medium size pores, show limited contents of large pores. With the lowest total pore volume at a level of 0.51 cm^3/g, and retention values of 65.5%, it is understandable that the sorption properties of fibers depend on the total pore volume and internal surface as well as on the character of the porous structure. An important issue is also the presence of capillaries in the external layer skin, which make it possible to transport moisture into the porous core. Owing to such a structure, moisture is absorbed by capillary condensation. The presence of the first, lower maximum (also for fibers containing MMT modified with aminododecane acid) in the pore distribution curve (Fig. 5) within the range of small pores corresponds with the values of moisture absorption at 100% RH at an average of 10–11%. The total content of small and medium size pores[5,7]

TABLE II
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)	(nm) Medium 15–75 (nm)	Large 150–750 (nm)	Very large 1875–7500 (nm)
M-149/1	−20	23.66	61.84	10.76	3.76
M-149/2	−5	27.05	54.11	11.11	7.73
M-149/3	+10	26.42	54.93	14.51	4.14
M-149/4	+25	27.07	46.78	16.97	9.17
M-149/5	+50	24.87	43.78	24.38	6.97

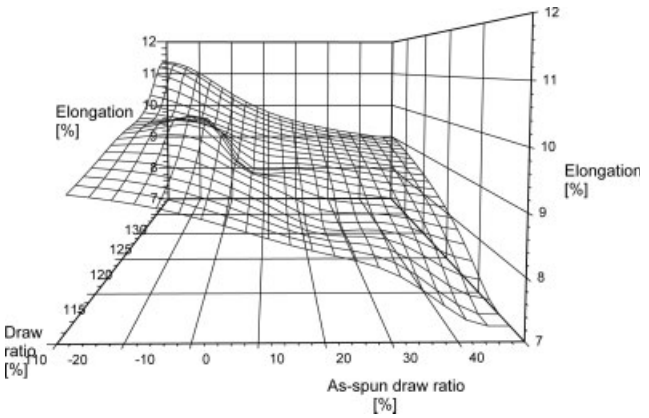

Figure 7 Dependence of fiber elongation at break on the as-spun draw ratio and total draw ratio.

(Table II) exceeding 39% qualifies all the PIA nanocomposite fibers (regardless of the MMT used) to the group of fibers with fine-porous structures. At the same time, the content of very large pores, that one structural defects affecting the fiber strength, is limited.

The fiber tenacity (Fig. 6) and elongation at break (Fig. 7) show a clear upward trend with the as-spun draw-out ratio changing toward negative values. The character of these changes is similar to that for PIA nanocomposite fibers containing MMT modified with aminododecane acid. Also the values of tenacity of fibers spun with comparable as-spun draw-out ratios are similar and range from 11.4 to 14.06 cN/tex. At the same time, they are higher by 3 cN/tex in comparison with PIA fibers containing Nanomer PGW which revealed a different character of changes in tenacity as a function of both variable process parameters.[5] A detailed interpretation of this phenomenon described on the basis of the specified type of MMT dispersion in the fiber-forming polymer, including the effect of MMT gallery subsidence (Nanomer PGW) found by us, has been given in this study.[6]

In light of these findings the following hypothesis seems to be probable: The higher tenacity of fibers containing MMT modified with octadecylamine is due to the disintegration of its agglomerates by the action of ultrasounds before adding to the post-reaction solution. The nanoadditive suspension in solvent (NMP) was treated with ultrasounds for 60 min at a temperature of ~25°C. Thus, it is necessary to assess with the WAXS method if this treatment has resulted in the exfoliation of MMT layers or if the previously mentioned phenomenon of MMT gallery subsidence takes place but with simultaneous decrease in their agglomeration. This question will be considered in the next paper concerning the effect of MMT quantity and type on the supermolecular structure and properties of PIA nanocomposite fibers.

CONCLUSIONS

1. The structure and properties of PIA nanocomposite fibers depend on the fiber spinning parameters, the presence of nanoadditive in the fiber-forming polymer as well as on the type of MMT modifier. The disintegration of agglomerates of MMT using ultrasounds can influence these parameters. The inverse effects of as-spun draw-out ratio and the extent of deformation during the drawing stage on the sorption and strength properties of fibers are observed.
2. The presence of MMT modified with octadecylamine in the fiber-forming polymer and the disintegration of MMT agglomerates by ultrasounds lead to a considerable increase in the internal surface and total pore volume, with the bimodal character of pore distribution curve being maintained. It results in 10% higher values of retention at lower sorption properties in comparison with PIA nanocomposite fibers containing MMT modified with aminododecane acid.
3. Regardless of the MMT modifier used (aminidedecane acid or octadecylamine), the PIA nanocomposite fibers show a similar level of maximum tenacity from 14 to 15 cN/tex (higher by 3 cN/tex in comparison with that of PIA fibers containing Nanomer PGW). This is probably connected either with the formation of additional secondary bonds between polymer macromolecules and the acid groups of MMT modifier or the disintegration of MMT agglomerates in the case of octadecylamine.

References

1. Mikołajc zyk, T. Fibres Textiles East Eur 2002, 10, 52.
2. Mikołajczyk, T.; Skwarski, T. Fibres Textiles East Eur 2002, 10, 14.
3. Mikołajczyk, T.; Skwarski, T. Fibres Textiles East Eur 2002, 10, 52.
4. Janowska, G.; Mikołajczyk, T. J Thermal Anal Cal 2003, 71, 549.
5. Mikołajczyk, T.; Olejnik, M. J Appl Polym Sci, in press.
6. Mikołajczyk, T.; Rabiej, S.; Olejnik, M.; Urbaniak-Domagała, W. J Appl Polym Sci, in press.
7. Mikołajczyk, T.; Olejnik, M. J Appl Polym Sci, in press.
8. Mikołajczyk, T.; Olejnik, M. Fibres Textiles East Eur 2005, 13, 24.
9. Mikołajczyk T. Scientific Bulletin of the Technical University of Łódź; No 781; Scientific Theses Z 243, Łódź, 1997.
10. Kacperski, M. Polimery 2002, 47, 801.