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Rheological Properties of Spinning Solutions of a Modified Polyimidoamide Containing Ceramic Nanoparticles

Abstract

The rheological properties of spinning solutions of a polyimidoamide modified by diaminodiphenyl methane in N-methylpyrrolidone containing silica nanoparticles or intercalated montmorillonite have been examined. The effects of adding nanoparticles on the rheological behaviour of the solutions examined are explained. It has been found that the incorporation of nanoparticles into the spinning solutions results in a more distinct non-Newtonian nature of the fluid, as well as a considerable increase in the rheological parameter k . The effect of the temperature of reheating the post-reaction solutions on the intercalation of montmorillonite and their rheological properties was also examined.

Key words: polyimidoamides, spinning solutions, rheological properties, silica nanoparticles, montmorillonite.

Introduction

The use of nanotechnology in textile engineering creates opportunities for increasing the functionality of fibres and imparting them barrier capabilities against the action of external factors.

The incorporation of ceramic (e.g. SiO₂) nanoparticles to a polymer during its synthesis or the preparation of its spinning solution makes it possible to produce fibres with these nanoparticles dispersed in the fibre-forming material.

The use of a laminar aluminosilicate leads to the formation of nanocomposite fibres that is characterised by the dispersion of intercalated montmorillonite in the fibre-forming material, and contains polymer macromolecules in the inter-layer spaces. It is necessary to make sodium montmorillonite hydrophobic, which is accompanied by an increase in the inter-layer distances. This facilitates the penetration of monomer molecules or polymer macromolecules into the inter-layer spaces [1].

Owing to their chemical composition, polyimidoamide fibres show a thermal resistance comparable with that of polyimide and aramide fibres, while at the same time serving as a barrier against the action of heat flux and flame (LOI at a level of 30) [2]. The incorporation of ceramic nanoparticles into the fibre-forming material can further improve these properties, and impart some new features to them, such as increased porosity and sorption properties resulting from that.

The major advantage of polyimidoamide fibres is that they emit very low quanti-

ties of smoke and practically no toxic decomposition products during their contact with flame. The synthesis of the fibre-forming polymer is environmentally friendly and proceeds at a low temperature, while the post-reaction solution can be directly used to spin fibres by the wet process [2,3].

The modification of the fibre-forming polymer by incorporating flexible segments of diamine or diaminodiphenyl methane [4-6] into the polymer chain brings about an increase in deformability and makes it possible, just after the stage of plasticising drawing, to obtain a tenacity of 15-16 cN/tex which is suitable for textile processing. At the same time, the fibres show a high thermal stability [7]. A further increase in the fibre tenacity may be expected, due to the possible formation of more secondary bonds between amide groups of the polymer macromolecules and the oxygen atom of montmorillonite. The formation of such bonds is found to be responsible for the tenacity increase in PA6 fibres containing montmorillonite [8]. On the other hand, both an increased porosity and improved sorption properties have been found in the case of fibres made from other fibre polymers containing silica nanoparticles [9]. The incorporated nanoparticles can also affect the rheological

characteristics of spinning solutions that are responsible for their processing into fibres by the wet process.

The aim of the present study is to assess the effects of two types of nanoparticles on the rheological properties of spinning solutions of a modified polyimidoamide in N-methylpyrrolidone. As is known, the value of parameter k depends on the intrinsic viscosity of the polymer and its content in the spinning solution. The value of this parameter can be also affected by the addition of MMT. In an extreme case, this may be a reason for correcting the technological parameters of the synthesis.

Object of Study

Post-reaction solutions of a polyimidoamide modified by diaminodiphenyl methane containing silica nanoparticles (solution A), or montmorillonite nanolamellae (MMT) (solution B) in amounts of 3% in relation to the polymer were subjected to rheological measurements as specified below.

Silica nanoparticles in the form of dispersion in a solvent were added to solution A (designated as solution after the reaction) at the initial stage of synthesis. For comparison, polyimidoamide was syn-

Table 1. Characteristics of nanoparticles. The SiO₂ used was produced at AGH in Cracow.

Type of nanoparticles	Size of particles, nm	Size of lamellae, nm	Distance between packets, nm
SiO ₂	50 - 150	-	-
Montmorillonite (Nanocoor PS)	-	800 x 550	2.3

thesised under the same conditions but without silica nanoparticles, as described in paper [10].

Montmorillonite (in the form of dispersion in a solvent) was added to solution B after the polymer synthesis was terminated. When the synthesis was completed, the polymer intrinsic viscosity was assessed, and in the case of satisfactory results, the solution was heated to determine the proper temperature for MMT addition. The stage of reheating in the technological process was not be used; the temperature of solution was lowered to the level found in the present study.

For comparison, post-reaction solutions synthesised under the same conditions, but without MMT, were also reheated. The characteristics of the nanoparticles of silica and MMT are given in Table 1.

Measurement Methods

The rheological measurements of post-reaction solutions of the modified polyimidoamide and the solutions containing nanoparticles of silica and MMT were

carried out with the use of a Rheotest RV rotary rheoviscosimeter and an H cylinder. The measurements were performed within the range of shearing rates up to 80 1/s at a temperature of 20°C. The parameters n and k were determined on the basis of flow curves given in the logarithmic system without including the shearing stress below 10 reading graduations, as it is known that for a polymer with a linear, quite rigid chain structure, at very low shearing rates, the orienting effect of this shearing can be negligibly small. The system structure is totally determined by Brownian motion, which causes a chaotic distribution of macromolecules. The internal friction of such a system will be constant and maximum. Furthermore, the power model of Ostwald de Vaele

$$\tau = k Y_x^n$$

where:

n, k - the rheological parameters of the model,

τ - the shearing stress,

Y_x - the shearing rate,

which is an approximate model, considerably better approximates the flow curves within the range of slightly higher shearing rates.

The limiting viscosity number $[\eta]$ was determined by extrapolating the reduced viscosity values to zero. The determination was performed at a temperature of 20°C. The content of fibre-forming material in the post-reaction solutions was determined on the basis of the weight of coagulated and dried films obtained from 1 g of solution.

The silica nanoparticles used were characterised by measuring their dimensions (for SiO_2 - the size of particles, for MMT the size of lamellae) with an electron microscope. In the case of the modified montmorillonite (the commercial product Nanocor PGW) the inter-layer distances were established on the basis of the position of the first peak in the WAXS X-ray diffractograms.

Results and Discussion

From the flow curves of the solutions containing silica nanoparticles and the solution without this addition (solution A, Figure 1) it follows that with similar values of intrinsic viscosity and polymer content, the solution without nanoparti-

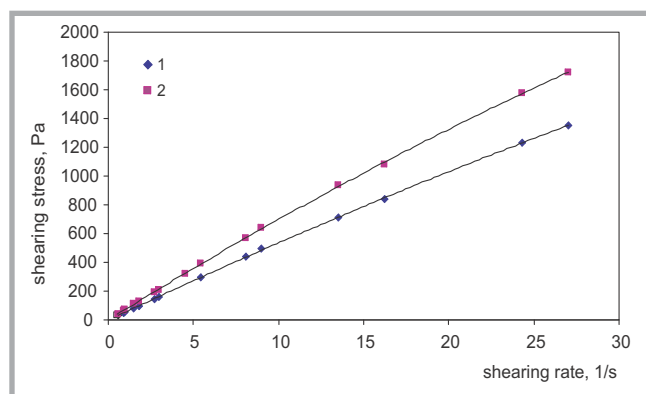


Figure 1. Flow curves of post-reaction solution (curve 1) and solution with silica nanoparticles (curve 2).

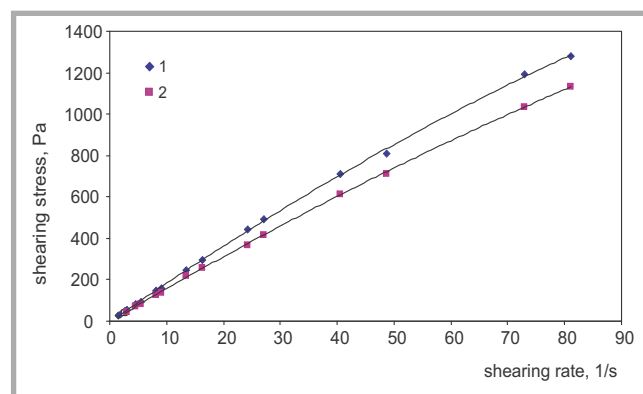


Figure 3. Flow curves of post-reaction solutions: curve 1 - reheating at 45°C, curve 2 - reheating at 150°C.

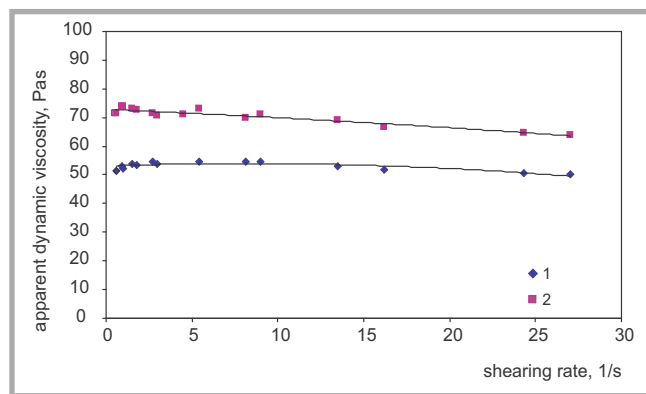


Figure 2. Dependence of apparent dynamic viscosity on the shearing rate of post-reaction solution (curve 1) and solution with silica nanoparticles (curve 2).

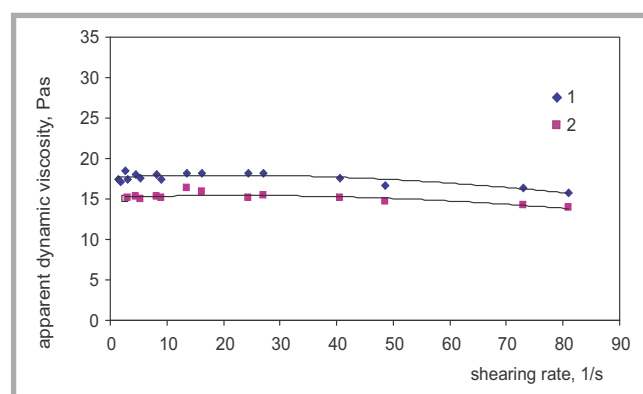


Figure 4. Dependence of apparent dynamic viscosity on the shearing rate of post-reaction solutions: curve 1 - reheating at 45°C, curve 2 - reheating at 150°C.

Table 2. Characteristics of spinning solutions.

Symbol of solution	Type of solution	Reheating temperature, °C	Intrinsic viscosity η , dl/g	Concentration, %	Apparent dynamic viscosity, Pas	Rheological parameters	
						n	k
A ₁	Post-reaction	-	1.0	24.25	52.38	0.99	53.54
A ₂	With silica nanoparticles	-	1.15	25.39	73.81	0.97	72.97
B ₁	Post-reaction	45	1.25	19.34	16.67	0.99	18.20
B ₂	Post-reaction	150	1.27	19.82	14.29	0.99	15.73
B ₃	With intercalated MMT	50	1.40	19.84	21.43	0.98	22.39
B ₄	With intercalated MMT	100	1.30	20.32	22.62	0.97	23.18
B ₅	With intercalated MMT	150	1.20	20.28	19.05	0.98	19.22

cles is a non-Newtonian liquid, but quite similar to a Newtonian liquid, slightly rarefied by shearing, without a flow limit. This is consistent with our previous findings [11]. The solution containing silica nanoparticles shows a typical character of a non-Newtonian liquid. Its rheological parameter n differs more from unity, and the solution is rarefied by shearing to a higher degree. The shearing stress increases less than proportionally with the increase in the shearing rate, and the flow curve is situated above an analogous curve of the solution without nanoparticles. Both solutions show a decrease in the apparent dynamic viscosity with an increase in shearing rate, which is typical for polymeric liquids (Figure 2).

A considerable increase in the parameter k is connected with the content of silica nanoparticles in solution A. A similar phenomenon is also observed in the case of solution B containing intercalated montmorillonite, but the increase in this parameter is smaller (Table 2).

From the flow curves (Figures 3 and 5), it follows that the solutions without nanoparticles, as well as those contain-

ing montmorillonite, regardless of the reheating temperature (in which were added MMT), are non-Newtonian fluids; these quite similar to Newtonian fluids, being only slightly rarefied by shearing, and their rheological parameter n is quite close to unity. All the solutions under investigation show a polymeric character. Their apparent dynamic viscosity decreases with the increase in the shearing rate (Figures 4 and 6).

Reheating the post-reaction solutions exerts practically no influence on their intrinsic viscosity. One can observe only a slight decrease in parameter k of the solution reheated at a temperature of 150°C, while the solution containing montmorillonite added at 50°C shows an increased intrinsic viscosity, i.e. a similar effect to the increase in the molecular weight of polymer. Thus, one may assume that in the post-reaction solution the macromolecules of polyimidoamide are situated between particular montmorillonite layers, and that an advanced intercalation of montmorillonite has taken place. At the same time, parameter k has a higher value in comparison with that of the post-reaction solution reheated at

a similar temperature, which corresponds to the difference in the value of apparent dynamic viscosity related to about 5 Pas of Hoeppler's dynamic viscosity. So, one may accept that due to the advanced distract of montmorillonite in the post-reaction solution, the temperature of 50°C is advantageous for addition, while 100°C seems to be the limiting temperature. On the other hand, the use of a higher temperature for reheating the post-reaction solution containing MMT may, due to increased molecular mobility, retard the formation of secondary bonds between the MMT layers and the macromolecules of polyimidoamide.

In accordance with the commonly accepted explanation of the phenomenon of rarefaction by shearing [12], the effect of nanoparticles on the mechanism of the system's rheological behaviour may be interpreted as follows:

In a stationary fluid, there is a considerable tangling of the macromolecules of the linear polyimidoamide, and the dispersed silica nanoparticles can be both inside these tangled macromolecules and between them. This effect can be further intensified by the tendency of nanoparticles to agglomeration. In the case of MMT, the layers of intercalated MMT are between the fragments of tangled macromolecules, which additionally increases the effective dimensions of macromolecules of immobilised continuous phase. During shearing, the polyimidoamide chains are straightened and disentangled. This effect becomes more and more pronounced as the shearing rate increases, causing a decrease in the internal friction of the system due to smaller dimensions of such molecules and less intensive interaction between

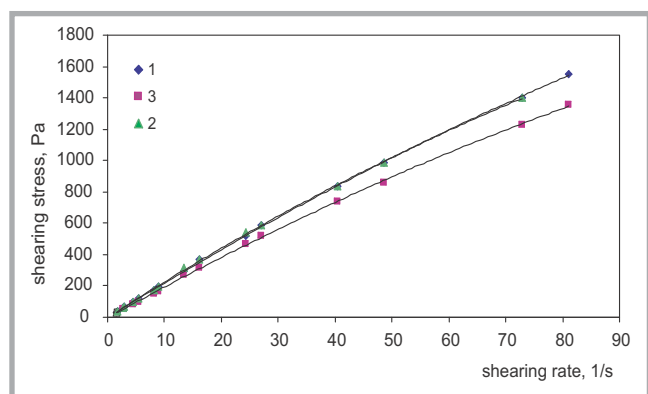


Figure 5. Flow curves of solutions with intercalated MMT: curve 1 - reheating at 45°C, curve 2 - reheating at 100°C, curve 3 - reheating at 150°C.

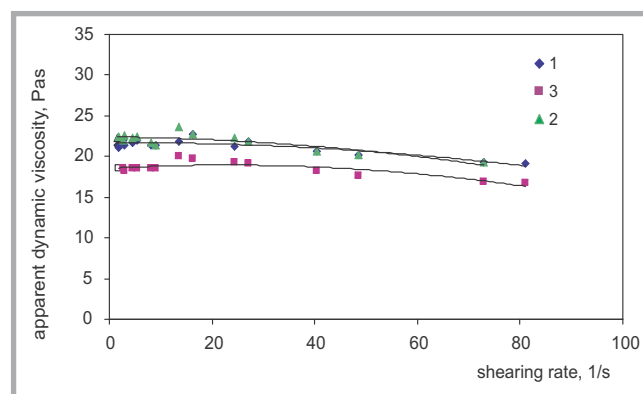


Figure 6. Dependence of apparent dynamic viscosity on the shearing rate of solutions with intercalated MMT: curve 1 - reheating at 50°C, curve 2 - reheating at 100°C, curve 3 - reheating at 150°C.

them. These interactions are also decreased due to the presence of silica nanoparticles or layers of intercalated MMT between macromolecules. The presence of nanoparticles in the system also exerts an influence on the course of rarefaction by shearing connected with solvation. The presence of silica nanoparticles facilitates a gradual tearing off of the solvation sheath with an increasing shearing rate, which also results in the decrease in the internal friction of the system. In the case of MMT, this effect may be weaker, while the presence of its layers with longitudinal and lateral dimensions of μm between the macromolecules of polyimidoamide definitely causes the polymer-solvent interactions to weaken. Thus, the incorporation of nanoparticles into the spinning solution affects the behaviour of the fluid, as is shown by the change in the rheological parameters n and k . The character of the fluid becomes more non-Newtonian, which is accompanied by a considerable increase in parameter k . This effect is more clearly seen in solutions containing silica nanoparticles than in solutions with intercalated MMT, which may be connected with the appearance of secondary bonds between oxygen

atoms in MMT layers and amide bonds of polyimidoamide macromolecules.

Conclusions

- The solutions of modified polyimidoamide in N-methylpyrrolidone containing silica nanoparticles or intercalated MMT are non-Newtonian fluids, rarefied by shearing without a flow limit.
- The addition of nanoparticles deepens the non-Newtonian behaviour of the fluid, and brings about a considerable increase in the rheological parameter k . This effect is more clearly visible in the solutions containing silica nanoparticles than in those with intercalated MMT.
- Due to the dispersion of intercalated MMT in the post-reaction solution, it is useful to introduce it at 50-100°C.

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References

1. M. Kacperski, *Polimery*, 47, No 11-12 (2002), 801.
2. Technical information about Kermel fibres from Rhone-Poulenc.
3. R. Pigeon, P. Pallard; *Die angewandte Makromol. Chem.* 40 (1974) 139.
4. T. Mikołajczyk, *Fibres & Textiles in Eastern Europe* 10(1), 52 (2002).
5. T. Mikołajczyk, T. Skwarski, *Fibres & Textiles in Eastern Europe* 10(3), 14(2002).
6. T. Mikołajczyk, G. Janowska, W. Urbaniak-Domagala, M. Szczapińska, *Fibres & Textiles in Eastern Europe* 13(1) 30 (2004).
7. G. Janowska, T. Mikołajczyk, *J. Thermal Anal. Cal.* 71, 549(2003).
8. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi, O. Kamigaito, *J. Polym. Sci., Part A: Polym. Chem.* 31, 1755-8 (1993).
9. T. Mikołajczyk, D. Wołowska-Czapnik, M. Boguń, *Fibres & Textiles in Eastern Europe* (in press).
10. T. Skwarski, J. Ratajczyk, T. Mikołajczyk, *Fibres & Textiles in Eastern Europe* 10(2) 35 (2002).
11. T. Mikołajczyk, T. Skwarski, *Fibres & Textiles in Eastern Europe* 9(4), 33 (2001).
12. J. Ferguson, Z. Kęmbłowski, *Applied Rheology of Fluids* (Łódź, 1995).

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