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Effect of MMT Content and its Modifier on the Rheological Properties of PIA Nanocomposite Spinning Solutions

Abstract
In this paper we have examined the rheological properties of spinning solutions of polyimideamide (PIA) nanocomposite containing different amounts of montmorillonite (MMT) in the form of the Nanomer PGW (produced in the USA), modified with aminododecane acid with octadecylamine. It has been found that regardless of the content and type of MMT, the solutions of PIA-MMT nanocomposite in N-methylopyrrolidone are non-Newtonian fluids rarefied by shearing without flow limit. The rheological properties of PIA nanocomposite spinning solutions depend not only on the content of MMT, but also on the type of its modifier.

Key words: *polyimideamide, montmorillonite, nanocomposite, spinning solutions, rheological properties, modifier.*

■ Introduction

The rheological properties of spinning solutions determine their processing ability and the final properties of the fibres. The dynamic viscosity of the solution (together with the feed rate and the receiving stress) influences the velocity distribution during the flow in the spinneret capillary, the course of relaxation processes in the off-spinneret zone and the value of crosswise velocity gradient changing along the fibre-forming path. The rheological properties of the solution also affect its spinning capability. If the dynamic viscosity is too low or too high, it can cause cohesive rupture or capillary decomposition. In the case of too high a viscosity, the use of an improperly selected receiving force can cause cohesive rupture, while too low a viscosity results in capillary decomposition. In the wet-spinning process from solution, both of these undesired phenomena can take place.

The rheological properties of spinning solution depend on the molecular weight of the polymer. At the same time, it is preferable to maintain a narrow curve of molecular weight distribution. In the case of the polyimideamide (PIA) which we used and also synthesised [1], these values are affected by the parameters of synthesis as the post-reaction solution is a spinning solution [1]. The incorporation of nanoadditive after the synthesis stage could require some correction of these process parameters. The characteristics of spinning solution (its concentration, the intrinsic viscosity of PIA and the apparent dynamic viscosity) also influence the course of spinning and appropriate selection of process parameters, on which the structure and properties of the fibres depend.

The characteristics of spinning solution and the chemical structure of the fibre-forming polymer also have a bearing on the polymer's susceptibility to the deformation processes taking place in the still fluid stream during its solidification. In the case of PIA, a polymer with a rigid macromolecular structure, this determines the effectiveness of the subsequent drawing process.

The effect of modifying polymer and spinning parameters on the structure and properties of PIA fibres has been analysed in some of our papers [2-6]. The incorporation of MMT into the post-reaction solution made it possible to obtain fibres with increased porosity and moisture absorption, together with a decreased flammability [7]. The strength properties of the PIA nanocomposite fibres were also dependent on the MMT's dispersion in the fibre-forming polymer, and on the type of modifier used to change the MMT hydrophilic properties to organophilic, i.e. compatible with the polymer and solvent used [8, 9]. The incorporation of MMT (Nanomer PGW) in a quantity of 3% in relation to the PIA solution in N-methylpyrrolidone resulted in a change in the rheological parameters n and k in comparison to the solution containing no nanoadditive. The non-Newtonian behavior of fluid and its polymeric character became more intense. The rheological parameter n was decreased, while parameter k increased [10]. These changes may be affected not only by the type of modifier, but also by the quantity of incorporated nanoadditive. However, it should be emphasised that detailed tests concerning the influence of different amounts of MMT in PIA have as yet not been carried out anywhere.

The aim of this study was to assess the effect of MMT quantity and type on the rheological properties of PIA nanocomposite solutions.

■ Materials and methods

We examined the spinning solutions of PIA [1] containing the following types of nanoadditives:
- MMT 'Nanomer PGW' (a commercial product from Nanocor, USA),
- MMT modified with aminododecane acid, and
- MMT modified with octadecylamine.

Both the modified MMT additives were prepared at the Institute of Industrial Chemistry, Warsaw. The characteristics of the nanoadditives used are given in [9, 11].

All the types of MMT were incorporated into post-reaction solutions in amounts of

1%, 3% and 5% in the form of a suspension in solvent, after being previously treated with ultrasounds at a temperature of 20 °C for 60 min to disintegrate MMT agglomerates. Polsonic 3-power equipment (Poland) was used, working at a power of 2×160 W, at a frequency of 40 kHz. The solutions containing 3% of Nanomer PGW or MMT modified with aminododecane acid had not yet been treated with ultrasounds.

The rheological measurements of PIA nanocomposite solutions in N-methylopyrrolidone containing variously modified MMTs were carried out with the use of a Rheotest RRV rotary rheoviscometer, using an H cylinder, within the range of shearing rates up to 80 l/s at 20 °C. The parameters *n* and *k* were determined from the flow curves presented in the logarithmic system, excluding the range of shearing rate below 10 read-out graduations. After all, it is known that in the case of polymer with a linear and quite rigid structure of chains, the orienting effect of this shearing may be negligibly low at low rates of shearing. The system structure is completely determined by Brownian motion that causes a chaotic distribution of macromolecules. The internal friction of such a system will be constant and maximal. Also the power model of Ostwald de Vaale

$$\tau = k \cdot \acute{Y}^n_x$$

where:

n and *k* – the rheological parameters of the model,
τ – the shearing stress, and
$\acute{Y}_x$ – the shearing rate,

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

Table 1. *Properties and rheological parameters of PIA nanocomposite spinning solutions; * - MMT incorporated without using ultrasounds.* **Remark:** *The properties of PIA without MMT are presented in [10].*

Symbol of spinning solution	Type of MMT	Amount of MMT, %/mass of polimer	Intrinsic viscosity [η], dl/g	Concetration of PIA spinning solution, %	Rheological parameters	
					„n"	„k"
152	Nanomer PGW	1	1,52	19.70	0.9869	23.720
141		3*	1,63	19.78	0.9895	29.597
153		5	1,37	20.08	0.9953	27.774
142	MMT modified aminododecane acid	3*	1,63	18.88	0.9891	38.410
157		3	1,26	20.06	0.9772	31.692
155		5	1,26	20.01	0.9466	35.460
151	MMT modified octadodecylamine	1	1,57	22.30	0.9732	42.304
149		3	1,53	20.04	0.9854	23.704
154		5	1,45	20.04	0.9830	22.908

The limiting reduced viscosity (viscosity number) [η] 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 polymer in post-reaction solutions was determined from the weight of coagulated films obtained from 1 g of solution.

MMT was characterized on the basis of plates dimensions taken by the method of electron microscopy. The inter-layer distances of variously modified MMT were determine on the basis of the first peak position in the X-ray WAXS diffractograms [8, 12].

■ Results and discussion

The characteristics of the solutions under investigation and their rheological parameters *n* and *k* are given in Table 1.

The concentration of PIA in the spinning solutions ranged from 19% to 20% except for the solution containing 1% of MMT modified with octadodecylamine. The

intrinsic viscosity was within the range of 1.4 – 1.65 dl/g, but that of solutions containing MMT modified with aminododecane acid was lower (1.26 dl/g), except for the solution containing 3% MMT, which had not yet been treated with ultrasounds to disintegrate the agglomerates.

Some discrepancy between the values of intrinsic viscosity was due to difficulties with adapting the synthesis parameters to the quantity and type of MMT to be incorporated (which required their correction). The influence of intrinsic viscosity differences will be taken into account in the detailed interpretation of changes in rheological parameters *n* and *k*.

From the analysis of flow curves (Figures 1, 2 and 3) it follows that regardless of the type and quantity of MMT, the solutions of PIA nanocomposite in N-methylpyrrolidone are non-Newtonian fluids rarefied by shearing without flow limit. The curves pass through the origin of coordinates, while the shearing stress increases less than proportionally with the increase in the shearing rate. All the
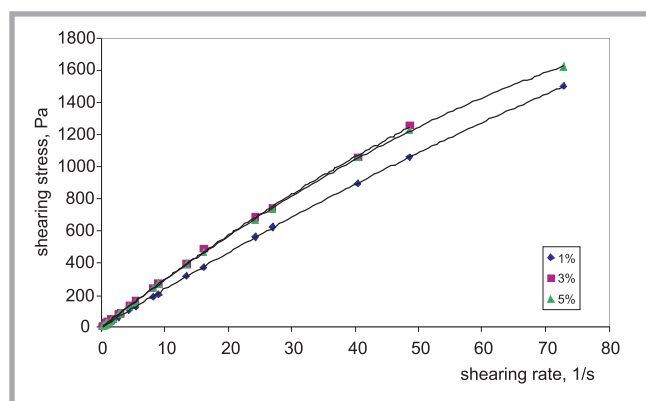

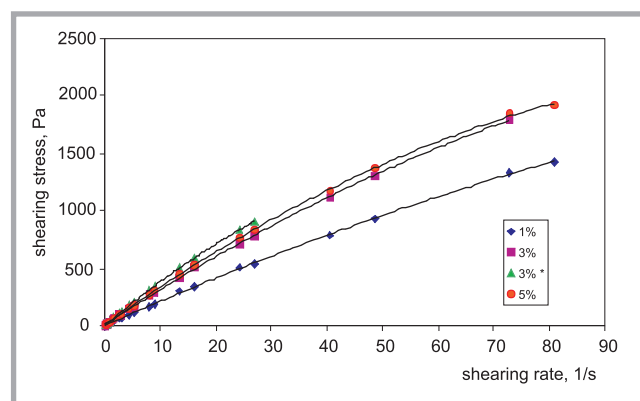**Figure 1.** *Flow curves of PIA post-reaction solutions with different amounts of Nanomer PGW.*

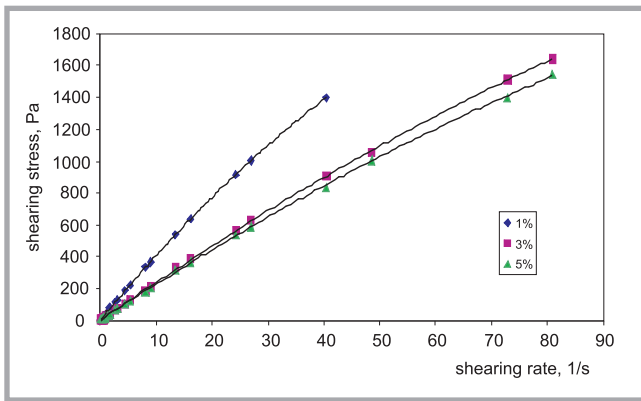**Figure 2.** *Flow curves of PIA post-reaction solutions with different amounts of MMT modified aminododecane acid.*

Figure 3. *Flow curves of PIA post-reaction solutions with different amounts of MMT modified octadodecylamine.*
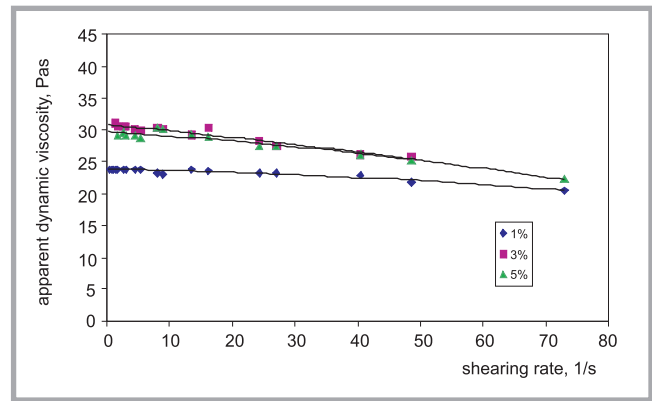

Figure 4. *Dependence of apparent dynamic viscosity on the shearing rate of PIA post-reaction solutions with different amounts of Nanomer PGW.*
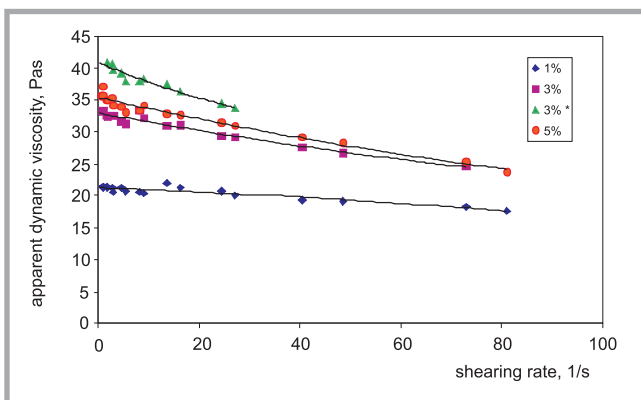

Figure 5. *Dependence of apparent dynamic viscosity on the shearing rate of PIA post-reaction solutions with different amounts of MMT modified aminododecane acid.*
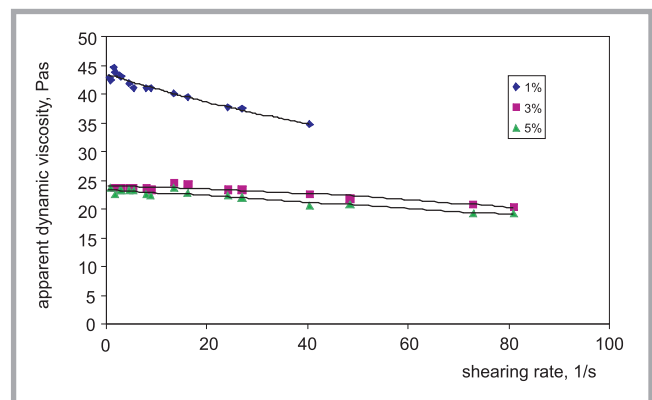

Figure 6. *Dependence of apparent dynamic viscosity on the shearing rate of PIA post-reaction solutions with different amounts of MMT modified octadodecylamine.*

solutions examined show a drop in the apparent dynamic viscosity which is typical of polymeric solutions, together with the increase in the shearing rate (Figures 4, 5 and 6). It is most noticeable for the solution containing 1% of MMT modified with octadecyl amine (solution 151), and for that containing 5% of MMT modified with aminododecane acid (solution 155). The drop mentioned is slightly less noticeable in the case of the solution containing 3% of Nanomer PGW. The solutions containing this type of MMT are also more similar to Newtonian fluids, especially the one containing 5% of Nanomer PGW, whose rheological parameter n assumes values of 0.9895 – 0.9953.

From the analysis of the effect of the nanoadditive content on the rheological properties of PIA solutions containing MMT modified with aminododecane acid, it follows that with the same values of intrinsic viscosity and concentrations of PIA differing by only 0.5%, the increase in the nanoadditive content is accompanied by a decrease in the rheo-

logical parameter *n* and an increase in the parameter *k*. Thus, the non-Newtonian behavior of fluid becomes more distinct. The rheological parameter n of the solution with an extremely high nanoadditive content decreases to the lowest value 0.9466, compared with those of all the remaining solutions. Thus, an effect appears which is similar to the increase in polymer molecular weight. Such behaviour by the solutions may also be connected with secondary bonds between the amide groups of PIA and acid groups of the modifier of MMT. An additional factor is the surface interaction of exfoliated MMT layers dispersed in the solution as a far-advanced or complete exfoliation was found (based on WAXS measurements) in the fibres obtained from solutions containing MMT modified with aminododecane acid [12]. The effect of exfoliation of the MMT packets which appear in the spinning solutions does not depend on the solution's concentration, which in this case (spinning solution 142) is different, like those of the remaining solutions of this group.

On the other hand, the solutions containing MMT modified with octadecylamine show a trend towards a decrease in parameter k, with small changes in parameter *n* when the nanoadditive content in them increases. The value of *k* is also affected by the variable value of intrinsic viscosity within the range 1.45 to 1.57 dl/g. The difference in behaviour from the previously described changes in the rheological properties of solutions containing this type of MMT may be also connected with the limitation of the MMT-polymer interaction only to surface interaction between aluminosilicate packages and PIA macromolecules, since in the fibres obtained from these solutions no exfoliation was observed [12]. The absence of exfoliation was also noted in fibres obtained from solutions containing Nanomer PGW. This is accompanied, as in the case of MMT modified with amine, by a decrease in the interlayer distances as indicated by the shift of the characteristic peak in the diffractogram towards higher values of 2θ. This testifies to a partial modifier 'passing' into the spinning solution [8].

The interpretation of the rheological properties of these solutions is made difficult by the fact that in preparing a solution with a Nanomer content of 3%, ultrasounds were not yet used to disintegrate the agglomerates, and so the solution's intrinsic viscosity was higher, amounting to 1.63 dl/g. From the comparison of rheological parameters n and k of solutions containing 1% and 5% of this MMT, it follows that these parameters increase with the increasing nanoadditive content.

The rheological properties of PIA nanocomposite solutions are also dependent on the type of MMT modifier. From the comparison of rheological parameters n and k of solutions with the highest nanoadditive content (5%) and similar values of intrinsic viscosity (1.26 to 1.45 dl/g) at the same concentration, it follows that the most non-Newtonian character is shown by the solution containing MMT modified with aminidodecane acid, the most similar to Newtonian fluid is the solution containing Nanomer PGW, and the solution containing MMT modified with octadecylamine occupies an intermediate position. The solution showing the most polymeric character (containing MMT modified with aminododecane acid) has the highest value of rheological parameter k, while in the other two solutions, this parameter decreases.

The chemical structure of the modifier has some bearing on the character of MMT-polymer interaction. When there are no strong interactions between the macromolecules of PIA and MMT, facilitating the exfoliation process, we can observe the influence of the ceramic nanoadditive on the decreasing polymeric character of the fluid.

In accordance with the generally accepted explanation of the mechanism of rarefaction by shearing [13], the effect of MMT on the mechanism of the system's rheological behaviour may be interpreted as follows. In an immobile fluid, a considerable entanglement of the linear polyimidoamide takes place, and the dispersed packages or particular layers of MMT can be both inside these entanglements and between them. The single layers or packages of MMT appearing between the fragments of entangled macromolecules bring about an additional increase in the effective dimensions of macromolecules with the immobile continuous phase. The

susceptibility to agglomeration may intensify this effect (despite the ultrasonic disintegration of the agglomerates) if there is a lack of complete exfoliation.

During shearing, the chains of PIA are straightened and disentangled. This effect becomes more and more distinct as the shearing rate increases, causing the system's internal friction to decrease thanks to the smaller dimensions of such molecules and the less intense interaction among them. These interactions are also limited by the presence of MMT layers or packages between macromolecules, especially when there are no secondary bonds between the modifier of MMT and polymer macromolecules.

The presence of MMT in the system also affects the course of rarefaction by shearing with solvation. The increase in the MMT content intensifies and facilitates gradual solvation sheath stripping with the increase in shearing rate, which is also accompanied by a decrease in the system's internal friction. The presence of MMT packages or layers with longitudinal and lateral dimensions of the μm order among the macromolecules definitely weakens the polymer-solvent interactions. The character of these interactions can be also affected by the type of modifier used to change the MMT properties from hydrophilic to organophilic. The addition of various quantities of MMT to the spinning solution brings about a change in the rheological behaviour of fluid, as confirmed by the change in rheological parameters n and k. The character of these changes depends on the type of modifier and the phenomenon of package exfoliation.

■ Conclusions

1. Regardless of the content and type of MMT, the solutions of PIA nanocomposite in NMP are non-Newtonian fluids rarefied by shearing without flow limit.

2. The increase in the content of MMT modified with aminododecane acid causes the non-Newtonian behaviour of fluid to become more apparent, and an increase in parameter k.

3. The rheological properties of PIA nanocomposite spinning solutions depend not only on the content of MMT, but also on the type of its modifier.

The character of these changes is affected by the presence (or absence) of exfoliation and the interactions between the macromolecules of PIA and MMT.

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