Application of a Linear Synthetic Polymer to Improve the Properties of Cellulose Fibers Made by the NMMO Process

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ABSTRACT: Low-molecular polyethylene (LMPE) as an internal flexibilizer was selected to improve the spinnability of cellulose solution in N-methylmorpholine-N-oxide (NMMO). It is compatible with the conditions of cellulose dissolution and fiber spinning because of its chemical stability and melting point. In the course of rheological investigations, it was proven that this modification has a physical characteristic. Cross sections of the fibers reveal that cellulose–LMPE forms a two-phase system with randomly distributed LMPE domains and a dominant skin-core structure. The addition of 5% LMPE is enough to improve significantly the mechanical properties of the fibers. An increase of LMPE above 5% worsens these properties, because LMPE is not a fiber-forming polymer. With the use of spinnerets with suitable dimensions, it is possible to obtain cellulose fibers with mechanical properties similar to those of synthetic fibers. The retention of water is lowered by the hydrophobic polyethylene polymer; however, it is high enough to retain the hydrophilic character of cellulose fibers. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2762–2773, 2002; DOI 10.1002/app.10227

Key words: cellulose; NMMO; low-molecular polyethylene; rheology; fiber properties

INTRODUCTION

The world's rapid population growth results in increased consumption of fibers, as they satisfy the basic requirements of the human being. It is considered that the present ratio of hydrophilic-to-hydrophobic fibers in use should be, at least, preserved. To sustain this trend, even at the most successful development of cotton or flax, a rapid growth in the production of manmade cellulose fibers is needed.

According to popular opinion, the N-methyl-morpholine-N-oxide (NMMO) process should completely replace the viscose method in the future production of manmade cellulose fibers, as an environmentally friendly technology without by-products, providing high-quality fibers and the prospect of mass production. Additionally, this approach creates quite a new possibility, for example, for the preparation of micro- and nanocellulose fibers.[1,2]

Some publications point to cellulose as a carrier of functional additives to produce special materials, for example, ceramic hollow membranes, ceramic fibers, electroconductive fibers, and bactericide or fungicide fibers.[3,4]

Cellulose derivatives can be spun from a liquid crystalline phase, which allows one to prepare fibers with very good mechanical properties.[5]

The content of organic or inorganic additives in the spinning dope prepared by the NMMO process can measure up to 700% in relation to cellulose, without any deterioration of its spinnability, and in this way, fibers with various applications can be prepared.[4]

To be realistic, however, despite these advantageous factors, it will take quite a lot of effort before this approach can be utilized.

The potential of NMMO as a solvent or cosolvent to prepare blends of cellulose and synthetic polymers was recently studied intensively to utilize the best properties of both cellulose and synthetic fibers. Actually, several synthetic polymers were blended with cellulose, such as poly(vinyl alcohol), polyacrylonitrile, poly(ethylene oxide), polyamide 6, polyamide 66, and copolyamide 6.69.[6,7,8]

In all these cases, a cosolvent is used, which creates new problems connected with miscibility and precipitation in coagulation systems.

Fibers made of mixed polymers have a great marketable value thanks to their improved mechanical and hygienic characteristics. This prosperous potential, however, has not been fully utilized in practice as yet.

Therefore, we tried to find such a polymer that would be the most suitable for the NMMO process. First, a cosolvent should be eliminated and second, the selected polymer ought to be suitable for the conditions of fiber preparation. These terms are fulfilled by the low-molecular polyethylene (LMPE), which was studied theoretically[9,10,11] and applied in practice as a polyethylene wax.

Commercially, polyethylene waxes are used in the processing of plastics as additives to polymers such as PE, PCV, or PP. They are also used in the manufacture of paints, increasing their abrasion resistance.

Polyethylene waxes added to the spinning solutions can facilitate the fiber formation process and make the produced fibers soft, owing to their action as internal plasticizers. Because of its melting point of 85–115°C, LMPE is compatible with the parameters of cellulose dissolving in NMMO and fiber spinning.

The suggestion to add polyethylene glycol with a molecular weight of 1.1 million to about 4.5 million of cellulose dissolved in a tertiary amino oxide to improve the flow rate in a spinning nozzle is described in U.S. Patent 5,047,197. WO 96/14451 discloses the use of poly(alkylene imine) derivatives to stabilize a shaped body derived from cellulose regenerated by the amino oxide process, and WO 86/05526 discloses the possibility of adding a number of polymers to a solution of lignocellulose materials in tertiary amino oxide.

However, none of these inventions presents a solution to the problem of significant fiber improvement by the amino oxide method as far as the strength, elongation, water absorption properties, and tendency to fibrillate are concerned.

Therefore, the aim of this study was to essentially improve such properties of the fibers produced by the tertiary amine oxide process, such as dry and wet strength, and elongation and reduction in the fibrillation. Moreover, the possibilities of controlling water absorption properties are also presented. Additionally, the rheological characteristic of the modified cellulose solution in NMMO is given as an essential part of polymer processing.

In the publication on rheological aspects of fiber formation from cellulose solution in NMMO, the method of reducing the disturbances in the spinning solution flow across the spinneret and extensional viscosity measurements by means of a capillary rheometer are described.[12] However, to entirely characterize such viscoelastic materials as cellulose solutions, it is necessary to perform dynamic oscillatory deformation experiments on cone-and-plate rheometer, which represents a way of measuring both viscous and elastic response.

The rheological behavior of cellulose solution in NMMO in dynamic measurements is depicted by Blachot et al.,[13] Petrovan et al.,[14] and Golova et al.[15] It concerns, however, the cellulose/monohydrate system and includes only unmodified solutions.

EXPERIMENTAL

All the cellulose solutions in NMMO were prepared in an IKAVISK blender (IKA-ANALYSEN-TECHNIK, Heitersheim, Germany). The operating volume of this apparatus is about 300 mL. It is equipped with recorders of temperature, stirrer, and torque moment counter (a measurement of torsional moment). These parameters are recorded by a computer.

To obtain reproducible results, all the experiments of dissolution of cellulose in NMMO were carried out according to the same procedure and the same dissolution parameters.

The cellulose solutions were prepared as follows. A weighed portion of thoroughly beaten cellulose was treated with a 60% aqueous solution of NMMO in such an amount that would provide the required concentration of the cellulose solution after the evaporation of excess water. The mixture of the aqueous solution of NMMO and cellu-

lose was transferred to the blender and then appropriate quantities of a stabilizer or other modifiers, prescribed for the given experiment, were added. The dissolution process was carried out at elevated temperature and under reduced pressure until an appropriate composition of the solution was obtained in the blender (i.e., until an appropriate amount of water was evaporated from the system). In addition to the proper composition, an important criterion of the solution quality was the appearance of the solution. The dissolution process was considered complete when the solution was transparent and homogeneous, and its surface was glossy.

Unfortunately, because of the lack of proper and fast analytical methods for evaluating the solution quality, the only reliable method was the experience of the person performing the experiment. The available literature offers descriptions of the evaluation of solution quality by the optical method[16] or by measuring its viscosity,[17] but according to our experience in this field, these methods fail to give good results, and in the case of more concentrated solutions (over 15%), they are practically unusable.

During the dissolution of cellulose, a change was observed in the viscosity of the system being stirred, and consequently, a change in the stirring resistance which could be recorded.

From the hitherto performed experiments, the changes in stirring resistances take place in a nonrandom manner and show the same or a very similar course in any process. At the final stage of dissolving cellulose in NMMO, after reaching maximum, the value of the torsional moment gradually drops. Then, the solution becomes homogeneous and its spinnability is best.

The method of recording the dissolution process does not require any sampling during the process. It is a direct method for an immediate and objective evaluation of the solution quality.

The hitherto performed experiments made it possible to establish and optimize the conditions for the dissolution of cellulose in the IKAVISK blender. From these experiments, the dissolution time is about 70 min for solutions containing 15% of cellulose. The final temperature of dissolution ranges from 120 to 130°C. It was established that optimal revolutions of the stirrer should be from 35 to 45 rpm. The process was carried out under vacuum [i.e., at about 24 kPa (180 Torr)].

Cellulose solutions in NMMO were prepared from spruce pulp with a polymerization degree (DP) of 680 and α-cellulose content of 93.5%. To the solutions with a cellulose concentration of 15%, the propyl ester of gallic acid (Tenox) as antioxidant was added in an amount of 0.5% in relation to α-cellulose. To improve the fiber properties, LMPE was selected.[18] It was put into the blender at the beginning of the cellulose dissolution process.

This product, with a polymerization degree of 4500 and a melting point of 98–108°C, is commercially available.

The fibers were formed by the dry–wet method by using 18-orfice spinnerets with dimensions of a diameter (d) of 0.16 mm and capillary length (l) of 0.64 mm and where d is 0.4 mm and l is 3.5 mm.

The detailed description of fiber spinning using cellulose solution in NMMO is given in ref.[19]

The temperature of the spinneret during the fiber formation was 115°C, and the distance between the spinneret and the surface of coagulating bath was 15 mm. Fibrillation degree was determined by means of the microscopic method in the so-called Shake Test.[20] To find out the internal structure of the prepared fibers as far as the phase separation is concerned, their cross sections were observed by means of a IEOLS scanning electron microscope.

Rheological measurements were performed on a Carri-Med cone-and-plate rheometer with a diameter of 20 mm and a gap of 0.2 mm.

RESULTS AND DISCUSSION

Rheological Characteristic

Two kinds of cellulose solutions in NMMO were used as testing materials:

15% cellulose + 0.5% Tenox as a thermal stabilizer

15% cellulose + 0.5% Tenox + 3.0% LMPE

The rheological experiments were carried out at temperatures in the range of 115–130°C, which allowed one to find the dependence of the rheological parameters on temperature under the conditions of fiber formation.

Steady-State Shear Flow

The investigated samples were sheared at temperatures of 120 and 130°C. In comparison to a capillary rheometer test, the shear rate was much lower and ranged from 0.2 to 253 s^{-1}. It is important to take measurements in a wide range of
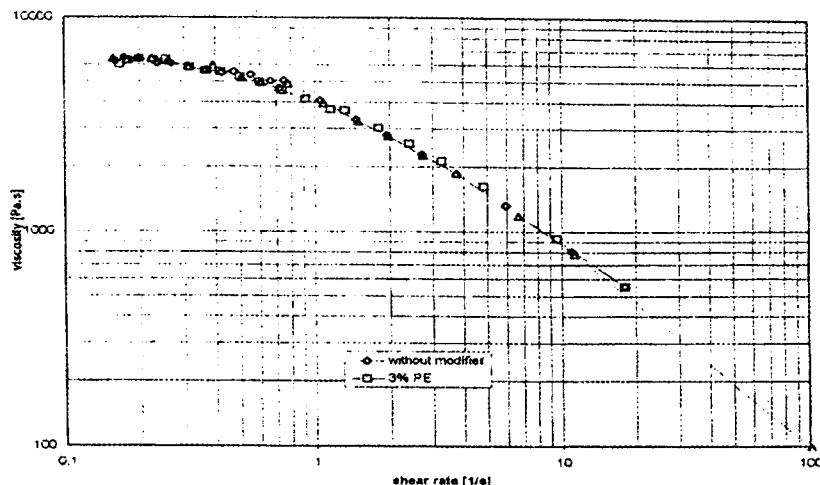
Figure 1 Shearing test at a temperature of 120°C.

shear rate, because at shear rates above 1000 s^{-1}, the polymer melt flows become unstable.[12] The Newtonian region is observed at a shear rate below $0.2–0.3 \text{ s}^{-1}$. Above this rate, the viscosity of the investigated solutions decreases quickly, particularly when the shear rate is higher than 1.0 s^{-1} (Figs. 1 and 2).

The samples show shear thinning, which is becoming stronger for the higher shear rate, showing their strong pseudoplastic behavior.

The curves of the investigated solutions coincide, especially visible for the shear rate above 1.0 s^{-1}.

Taking this phenomenon into account, the dependence of viscosity on temperature at the stated rate of 1.0 s^{-1} is shown in Figure 3.

The solutions modified by LMPE have distinctly lower viscosity than a pure solution. It may be caused by the slipping effect; the macromolecules become more moveable, and in this way, LMPE acts as an internal flexibilizer. The influence of LMPE on the viscosity above shear rate of 1.0 s^{-1} is masked by shear thinning. The deformability of the solutions with a higher amount of LMPE will be tested in the spinning experiments. For the complete characterization of the cellulose solution in NMMO, it is necessary to calculate the characteristic flow index from the power law equation and activation energy.

The Calculation of the Characteristic Flow Index

To quantify the pseudoplastic behavior of the cellulose solutions in NMMO, the power law equation is suitable, as follows
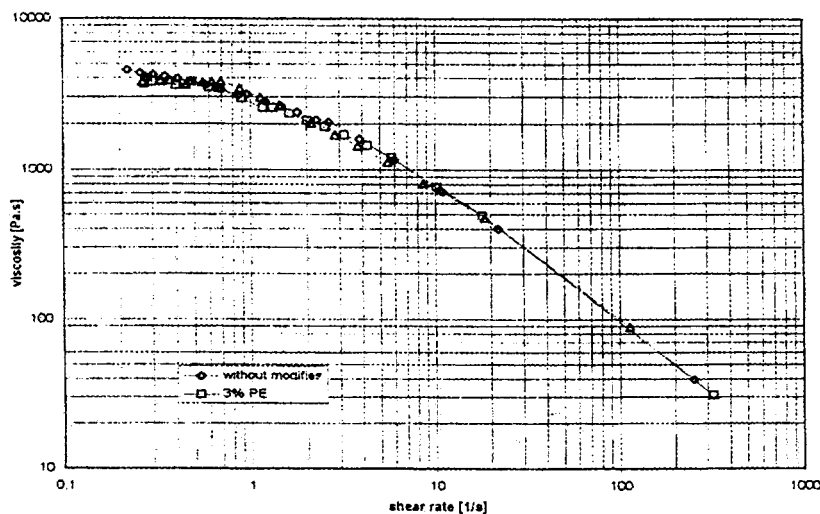
$$\delta = \eta \dot{\gamma}^n \qquad (1)$$

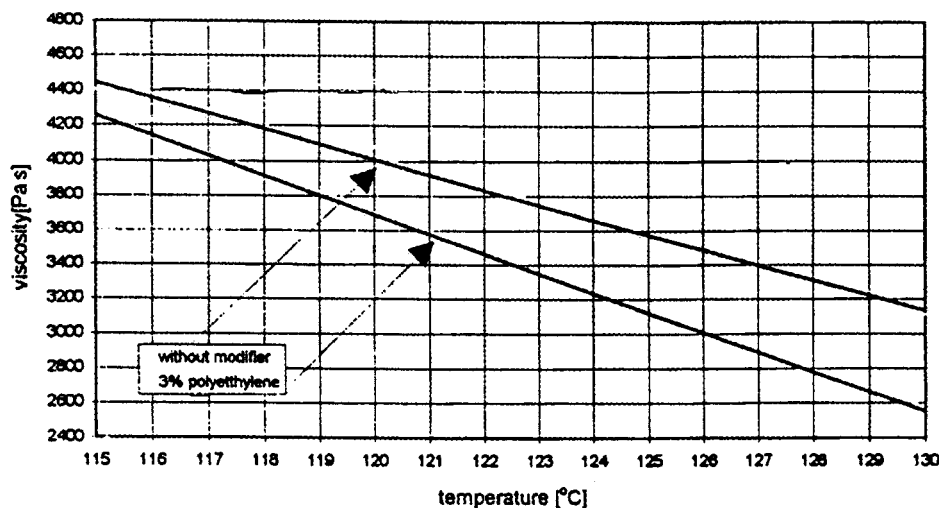**Figure 2** Shearing test at a temperature of 130°C.

Figure 3   Viscosity versus temperature at shear rate of $1.0\ s^{-1}$.

Experimentally, n is obtained from the plot log δ against log $\dot{\gamma}$ before any corrections are made. For Newtonian fluids, it amounts to one, and the smaller it is, the more the fluid differs from the reference. The results are given in Table I. Table I indicates that with the increase of the deformation rate, the fluids become more and more non-Newtonian and this fact should be taken into account during the processing of the investigated material.

The Calculation of Activation Energy

When the natural log of the polymer viscosity is plotted against $(1/t)K^{-1}$, an Arrhenius plot is obtained. The slope dependence of this plot gives flow activation energy. The mathematical expression for the Arrhenius' equation is

$$\eta_0 = Ae^{Ea/RT} \qquad (2)$$

where $R = 8.3142$ J/mol K is the universal gas constant and Ea is the activation energy, KJ/mol. Then

Table I   Characteristic Flow Index n

Composition of the Solution	Shear Rate	
	$<200\ s^{-1}$	$200\text{–}1000\ s^{-1}$
15% Cellulose solution without modifier	0.72	0.60
15% Cellulose solution + 3% LMPE	0.53	0.44

$$\mathrm{In}\,\eta_0 = \mathrm{In}\,A + \frac{E_a}{R}\frac{1}{T} \qquad (3)$$

where A is the viscosity coefficient, in Pa s, and E_a/R is temperature coefficient, in K.

The activation energy is calculated from the temperature coefficient. It is well known that activation energy depends on shear rate. This problem can be eliminated when the Newtonian viscosity is chosen to make an Arrhenius' plot. Because Newtonian viscosity is difficult to measure, the computer extrapolation methods were used to obtain this viscosity from flow curves for temperatures of 110–130°C. The results are given in Table II.

The addition of polyethylene causes the activation energy to increase because this polymer has a higher melting point than the unmodified cellulose solution in NMMO (60°C).

The Creep Test

When a body is subjected to a constant stress it will deform in different ways controlled by its modulus. As the stress is removed after a certain time, not all the strain is recovered. The amount of unrecovered strain is called a permanent set. This test is known as a creep test. Frequently, the creep curve is plotted as the strain divided by the imposed stress. This ratio is a compliance as a reciprocal of elastic modulus and it characterizes the body's ability to deform. In this way, the flexibility of the macromolecule chain can be described.

The creep tests were carried out at a temperature of 115°C (i.e., at the temperature of fibers

Table II   The Activation Energy of the Solutions

No.	The Resulting Value	Solution	
		15% Cell. + 0.5% Tenox	15% Cell. + 0.5% Tenox + 3% Polyethylene
1	Viscosity coefficient, Pa s	0.3563	1.193×10^{-3}
2	Temperature coefficient, K	3644.2	5450.9
3	Regression	0.98	0.99
4	Activation energy, (kJ/mol)	30.2	45.2

formation). The following cellulose solutions were tested:

15% cellulose + 0.5% Tenox

15% cellulose + 0.5% Tenox + 3% polyethylene

The results are depicted in Figures 4 and 5.

The curves have similar shapes. The deformations have a high-elastic character with almost an instantaneous response of the strain recovery component. It can be interpreted as the straightening of the 1,4-glicoside bonds in the chain of the cellulose macromolecules and their parallelism in the amorphous area. It is also probable that there is a change of macromolecule conformation by rotation of the bonds in the main chain without any of the valence variation angles and interatomic distances.[11] The investigated solutions have much smaller compliance than carboxymethyl cellulose solution,[21] which is understandable, taking into account the concentration of both materials. The positive influence on deformability of the solution with LMPE is visible; the compliance of the unmodified solution is lower than 0.008 m^2/N, whereas for modified solutions it is higher than 0.008 m^2/N.

Dynamic Test

The dynamic deformation provides information on viscoelastic properties of the tested material.

Storage modulus G' is a measure of storage energy (elastic response), and loss modulus G''
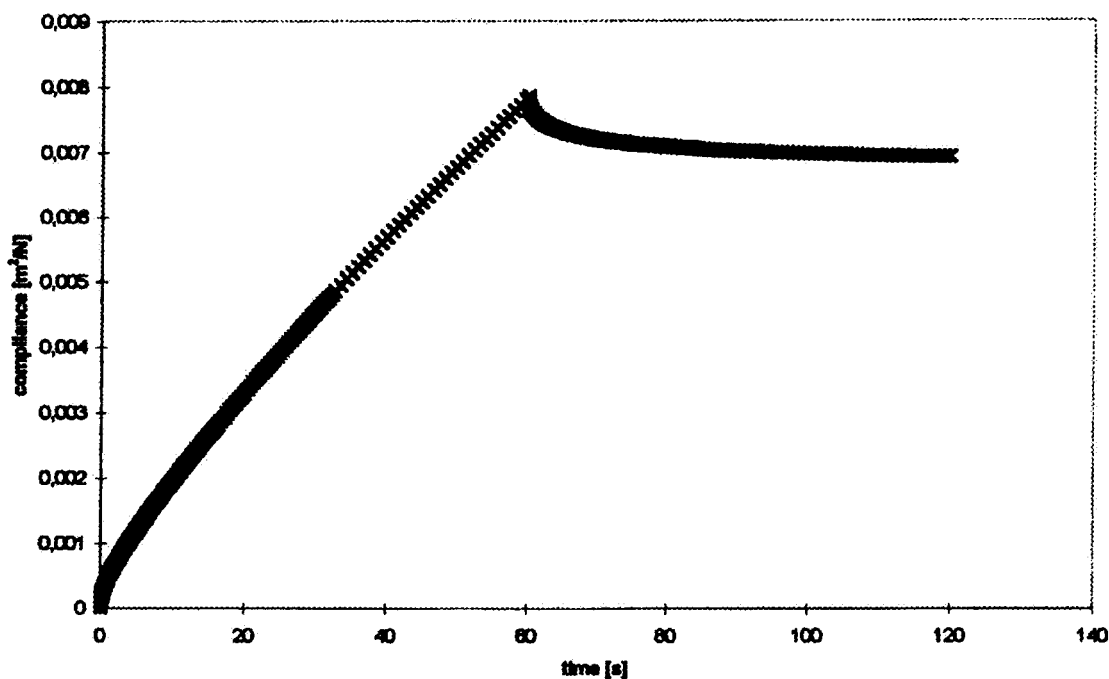

Figure 4   Creep test at a temperature of 115°C. Unmodified solution.
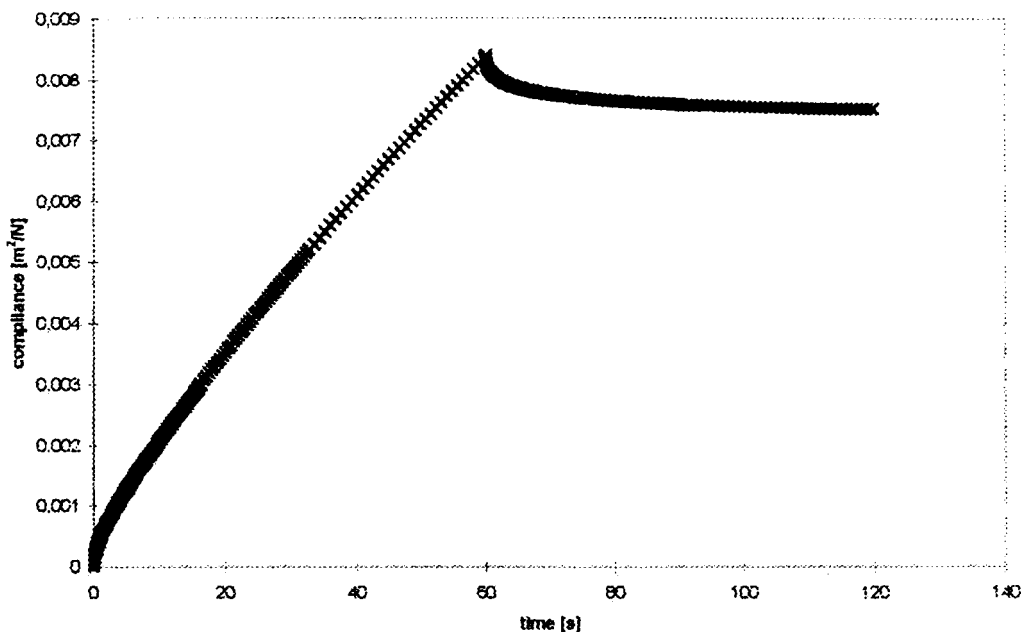
Figure 5   Creep test at a temperature of 115°C. Solution modified by polyethylene.

indicates the amount of energy transformed into heat (viscose response). The storage or elastic modulus can be defined according to the equation,[22]

$$G^{\bullet} = G' + iG'' \qquad (4)$$

where $G^{[\text{chempt}]}$ is the total resistance of a substance against the applied strain.

The effect of dissipation energy can also be described by means of viscosity as a result of dividing loss modulus G'' by angular frequency. In this way, the real part of the complex viscosity known as dynamic viscosity is obtained as

$$\eta' = \frac{G''}{\omega} \qquad (5)$$

where η is the dynamic viscosity, and ω is the angular frequency in rad/s.

A very useful dimensionless parameter, being a measure of the relationship between the loss energy and storage energy, corresponding to the capacity of material to waste energy, is known as a loss angle tangent or the internal friction coefficient:

$$tg\,\delta = \frac{G''}{G'} \qquad (6)$$

The variations of storage modulus G', loss modulus G'', and dynamic viscosity η' versus frequency in rad/s at a temperature of 115°C are shown in Figures 6 and 7.

The figures are plotted in natural scale for easier interpretation of the phenomena in the course of dynamic deformation.

The tested fluids are shear thinning, as was already observed during shearing experiments.

A strong decrease in the dynamic viscosity is noticed at a frequency of 20–30 rad/s; then the decrease is much lower. Macromolecules become parallel up to a certain position when the further movement is restricted by the generation of intermolecular bonds. It is also seen from the value of storage and loss moduli that they initially differ slightly and when the strain becomes higher, the loss modulus has almost constant value, but during that time the storage modulus increases constantly. At the high deformation, the elastic properties of the fluid have decisive meaning. This is important for fiber spinning because elastic properties are strictly connected with the deformation of the fibers being spun. The shapes of the curves characterizing the dynamic properties of the tested samples are similar. It means that the examined modifier does not affect the internal structure of cellulose solutions and no derivatives are formed. It is self-evident from the chemical constitution of the applied substance.
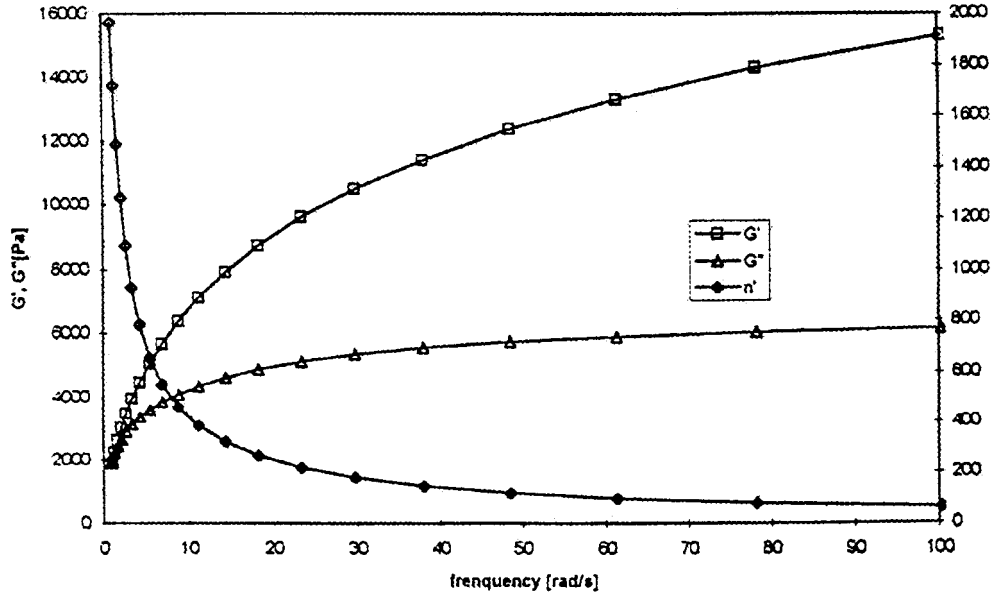
Figure 6 Dynamic test at a temperature of 115°C. Unmodified solution.

On the grounds of modulus measurements, the calculations of the internal friction coefficient $tg\delta$ were also made. The results are presented in Figure 8.

The drop in $tg\delta$ is very quick at frequencies of 20–30 rad/s, and the deformation takes place mainly in the amorphous phase. During the deformation process, the amorphous phase will be first deformed to accommodate the applied stress.

When the amorphous chains are strained, they will either rearrange and reinforce one another to pull the crystalline region or they will fracture. In the amorphous region, the chains have enough free volume to permit translation. For a higher strain, the deformation has an elastic character which determines the fluid properties.

The shapes of the curves of the investigated solutions are similar, which means that the mod-
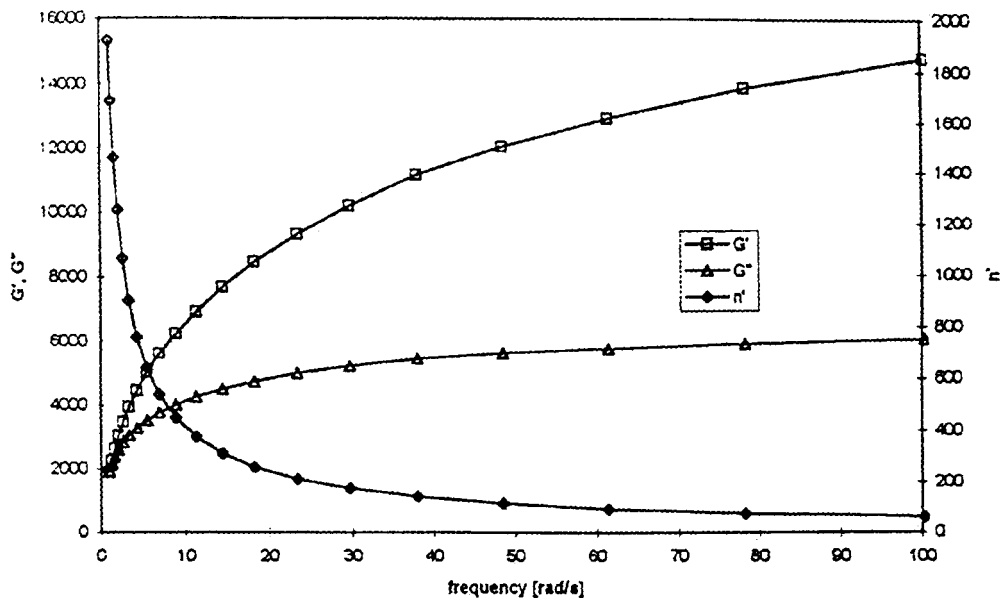

Figure 7 Dynamic test at a temperature of 115°C. Solution modified by polyethylene.
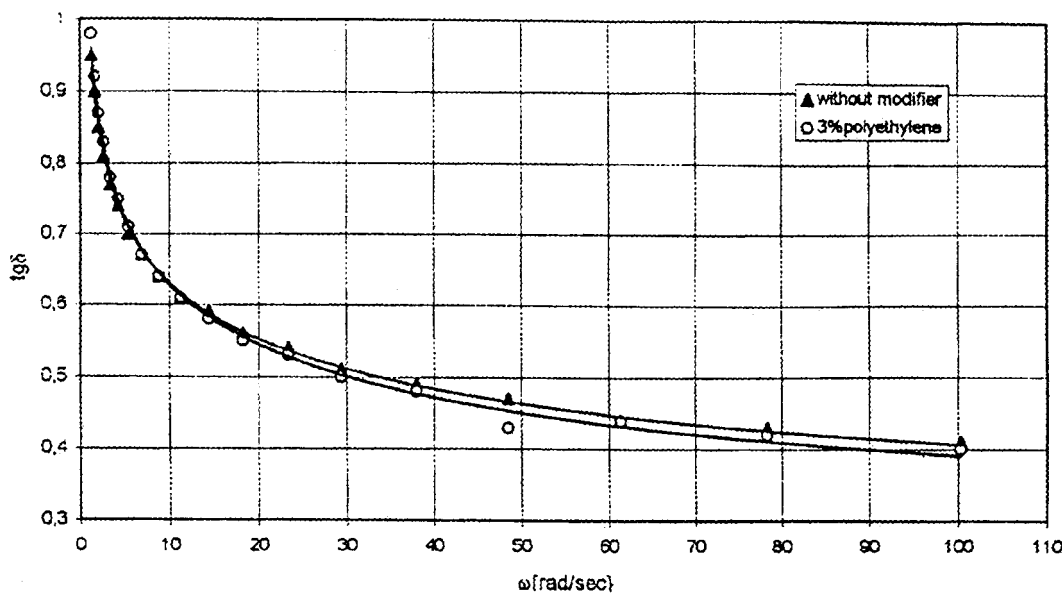
Figure 8 Internal friction coefficient versus angular frequency.

ification of solutions has not influenced their chemical structure.

On the basis of the performed rheological experiments, one may conclude that the modification of the cellulose solution by LMPE improves the movability of the macromolecules and their aggregates. In this way, it facilitates the process of fiber spinning.

Fiber Spinning

With the use of spinning solutions containing 15% of cellulose and various amounts of LMPE, fibers were spun with a constant (2.0 m/min) flow rate of the spinning solution through the spinneret capillary. The samples of the fibers were taken at the maximum draw ratio at which elementary filaments were broken.

This factor as a ratio of the fiber spinning rate to the flow rate of solution through spinneret can be regarded as deformability in the shearing flow. This is one of the two components describing the solution spinnability, whereas the second one is the deformation ability in the extensional flow.[12]

The properties of fibers spun with the spinneret 0.16 × 0.64 mm (diameter × length) are given in Table III.

From the results, it is evident that the presence of LMPE in an amount of 5.0% in relation to α-cellulose has a positive influence on the deformability of the cellulose solution in NMMO as a consequence of the slipping between the macro-

molecular chains and supermolecular polymer elements or the slipping of the boundary layer.

LMPE affects the fiber strength, elongation, and fibrillation. Moreover, the retention of water is lowered by the incorporation of the hydrophobic polyethylene polymer. When the amount of LMPE exceeds 10%, the mechanical properties of the fiber become gradually worse, because this additive apparently does not have fiber-forming ability.

The capability of LMPE to improve fiber properties was especially clear after the experiments in which the spinneret with dimensions of 0.16 × 0.64 mm was replaced by a spinneret with dimensions of 0.4 × 3.5 mm. The use of a spinneret with an increased capillary length to diameter ratio (l/d) has a positive effect on the solution orientation and in the spinneret and consequently on the fiber properties[12] (Table IV).

Cross Section of the Fibers Modified with LMPE

The cross section of the fibers under investigation is shown in Figure 9. Cellulose and polyethylene create a two-phase system; continuous phase is formed by cellulose and the inclusions consist of polyethylene domains, the size and distribution of which are very irregular. Miscibility of the cellulose–LMPE system was proven by plotting the storage modulus (G') against the loss modulus (G'').[23] The curves coincide with each other, which testifies to the blend compatibility (Fig. 10)

Table III Properties of Fibers Containing Low-Molecular Polyethylene (LMPE)

No.	LMPE by Weight of Cellulose (%)	Linear Density (dtex)	Tensile Strength (cN/tex)	Elongation at Break (%)	Wet Tensile Strength (cN/tex)	Loop Tensile Strength (cN/tex)	Wet Elongation at Break	Relative Strength (%)	Water Retention (%)	DP of Cellulose Fibers	Fibrillation Degree	Deformability of the Spinning Solution
1	2	3	4	5	6	7	8	9	10	11	12	13
1	—	3.19	24.5	11.8	18.3	6.0	18.5	74.0	81.3	664	6.0	1820
2	3.0	3.05	25.0	9.6	21.4	5.6	14.9	85.0	80.6	660	3.8	1950
3	5.0	2.13	32.0	12.2	25.7	8.9	16.4	80.3	79.4	661	3.8	2090
4	10.0	2.59	29.4	11.9	24.0	7.6	14.6	81.6	76.8	601	4.3	1525
5	15.0	2.83	27.1	13.2	21.8	7.6	17.2	80.4	66.3	559	4.5	1530

The "Fiber Properties" spans columns 3–12.

Table IV Properties of the Fibers Modified with LMPE and Spun with the Spinneret 0.4 × 3.5 mm

Example	LMPE by Weight of Cellulose	Fibers Properties		
		Linear Density (dtex)	Tensile Strength (cN/tex)	Elongation (%)
1	—	3.64	44.54	7.04
2	5.0	2.06	54.76	6.46

It this case, however, the polyethylene phase dominates on the fiber surface by producing a sort of skin-core structure. It may be the shearing effect or the phase separation, although there is no systematic mechanical theory that deals with this phenomena.[24] More probably, it results from the difference in density, which is 1115 g/cm^3 for cellulose solution in NMMO against 0.89 to 0.91 g/cm^3 for LMPE.

CONCLUSION

LMPE is a suitable agent to modify the fiber spinning from cellulose solution in NMMO.

LMPE is a stable compound under the conditions of cellulose dissolution and fiber spinning. Its melting point is compatible with the temperature of fiber formation, thus eliminating the necessity of using cosolvent.
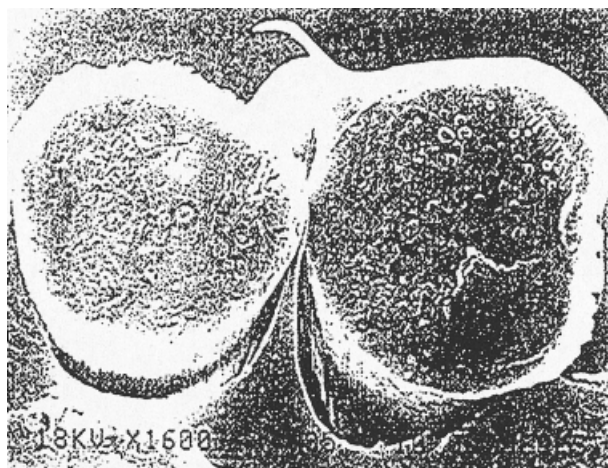

Figure 9 Cross section of cellulose fibers spun from the spinning solution containing polyethylene. Magnification, ×1600.
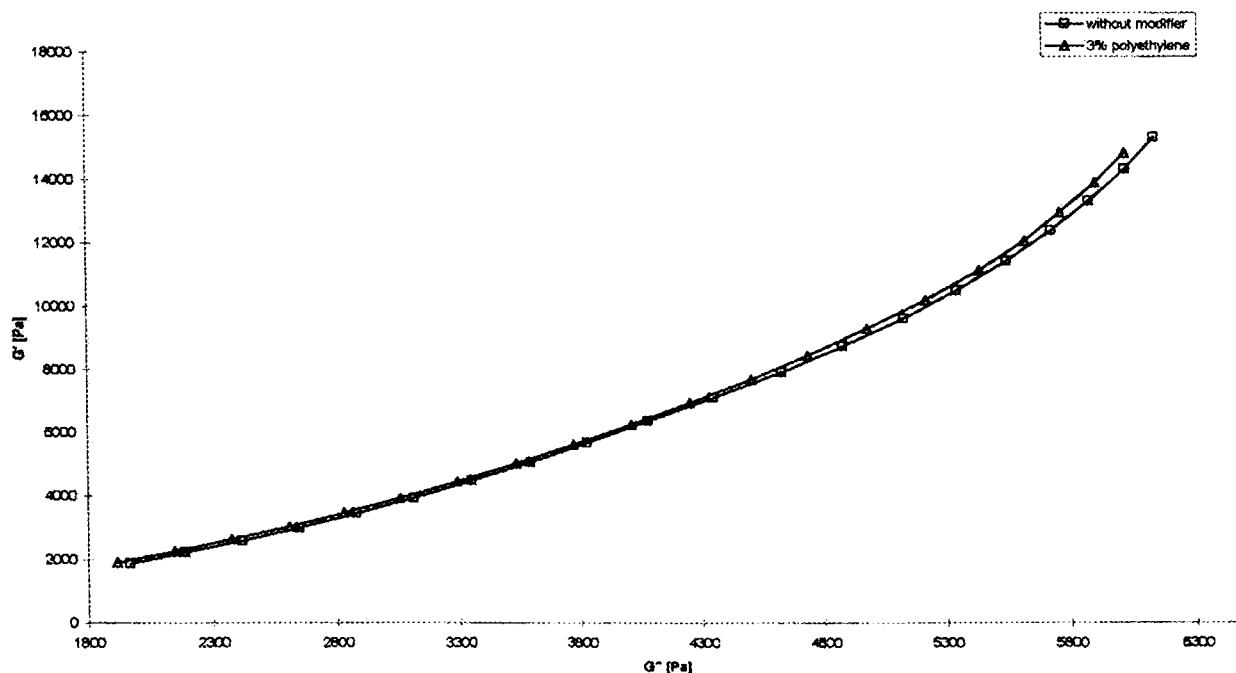
Figure 10 Storage modulus against loss modulus for solutions unmodified and modified by polyethylene.

The modification has a physical character owing to the chemical constitution of the applied modifier. The cross section of the fibers reveals a two-phase system: inclusions of LMPE domains in continuous cellulose phase with random distribution. The layer of LMPE is visible on the fiber surface, mostly because of the difference in density between these two components. This conclusion is also supported by rheological examinations. LMPE does not affect the internal structure of pure cellulose solution, because both the storage modulus responsible for the elastic response and the loss modulus responsible for the viscose response have similar powers in relation to modified and unmodified solutions. It is confirmed by the shapes of curves of internal friction coefficient (*tg*).

In the shearing flow, the addition of LMPE decreases the viscosity of the cellulose solution thanks to the slipping of structural elements of the system and the formation of a boundary layer. This factor facilitates the deformation of solution in the spinneret channel, which produces the desired effect with respect to the mechanical properties of the fibers.

The addition of the 5% LMPE is enough to improve significantly the fibers of tensile strength and loop strength. In this way, it is possible to increase the fiber strength by using a spinneret with a high *l/d* ratio.

A further increase in the LMPE content in spinning solutions leads to the worsening of the mentioned properties, because this additive is not a fiber-forming polymer due to its molecular weight.

The retention of water is lowered by the hydrophobic polyethylene polymer, but it is high enough to preserve the hydrophilic properties of cellulose fibers.

Generally, one can state that LMPE in a limited amount is compatible with the parameters of fiber spinning by the NMMO process, acting as an internal flexibilizer, which significantly improves the mechanical properties of the resultant fibers.

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