

Quantum-chemical simulation for production technologies of high-strength Zylon fibers

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Abstract. Using computer simulation methods, the geometry of the blocks that make up the Zylon polymer chain was established, the impossibility of the existence of a strictly linear polymer was shown, as well as the rotational barrier of the conformational transition of the benzobisoxazole block. computed. An assumption was made about the possibility of the transition of Zylon into various conformational states when creating high-strength fibers.

1 Introduction

Prospects for the creation of modern transport systems are associated with the development and use of high-strength heat-resistant composite materials (CM) [1-3].

A method for predicting the durability of a composite based on the kinetic theory was proposed in the work [4]. In this work, we study the geometry and conformational transitions of the polymer chain of Zylon, an ultra-high-strength material for technologies for the production of new CMs.

Currently, a wide range of composite materials based on carbon, fiberglass and aramid yarns and fabrics, polyethylene compositions, polyvinyl chloride plastic compounds, polyurethanes, and polyamides are actively used in aviation and space technology.

Among all organic fibers, aramid yarns are widely used and have the highest performance characteristics (strength, modulus of elasticity). They are resistant to flames, high temperatures, organic solvents and petroleum products.

For the production of power elements, basalt fiber is used, which is produced from various rocks of similar chemical composition – basalt, basanites, amphibolites, gabrodiabases or mixtures thereof.

One of the most promising polymeric structural materials is ultrahigh molecular weight polyethylene (UHMWPE). Ultra-high molecular weight polyethylenes include polyethylenes with a molecular weight of over 1,000,000 g/mol, which have a unique set of physical and mechanical properties and are in demand in various fields due to their high

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wear resistance, low friction coefficient, high impact strength, and low brittleness temperature (up to -200°C).

Another common group of high-strength materials are carbon-based materials, from which carbon fibers and composites based on them are made. Carbon fibers are the main material for the production of threads and fabrics, as well as high-strength cables for large-scale ground-space systems, which include orbital tether systems and a hypothetical space elevator [5-7].

Cable elements require a material with very high specific strength and low mass density. As such a material, carbon nanotubes and other carbon modifications are traditionally considered due to their high characteristics. Theoretical calculations have shown a tensile strength of over 130 GPa, which is more than 40 times the strength of alloy steel.

The density of nanotubes is about 6 times less than the density of steel. Specific tensile strengths were determined: for carbon nanotubes – 46268 kN·m/kg [8], for other carbonaceous materials – from 2400 to 62000 kN·m/kg. However, with the large-scale production of fibers and products made from them, it is impossible to avoid atomistic defects of various sizes and shapes that significantly reduce operational characteristics (strength, fatigue, elasticity, etc.) [9].

It should also be borne in mind that carbon fibers have a tendency to oxidize in air, chemical activity when interacting with metal matrices, and relatively weak adhesion to polymer matrices, which requires additional surface treatment of the fibers to increase their adhesion. Therefore, the further development and subsequent application of new polymeric materials with increased strength and low specific gravity seems relevant. When choosing a material, first of all, it is necessary to take into account the possible change in its strength properties as a result of the influence of humidity, radiation, variable wind load, sudden temperature changes, etc.

At present, composites consisting of high-strength polymer fibers and a soft matrix are widely used. The main load is assumed by the fibers, and the matrix provides an even distribution of the load between the fibers. Such materials with the greatest strength include: Vectran, Kevlar, polyethylene, etc. These materials are already actively used in a number of areas, but also in the literature there are many new works expanding the potential of their use.

The most durable and high-performance structural materials are polymer fibers with highly oriented macromolecules. There are many ways to obtain high performance polymer fiber. A common industrial method is to draw a polymer or oligomer melts through a thin die, followed by cooling and winding onto spools. However, this method is not well suited for the production of fibers from thermoset polymers and from polymers with a high melting point.

The easiest way to implement highly oriented fibers is electrostatic spinning, or electrospinning. In this process, the fiber is formed as a result of the action of electrostatic forces on an electrically charged stream of polymer solution or melt.

Yaqian B.J.L. et al. [10] describes of the production of heavy-duty Kevlar-based fibers (specific tensile strength 2514 kN·m/kg) and technology for the production of fibers with various stiffness characteristics based on the regulation of the fiber diameter during wet spinning. A hydrophobic Kevlar fiber (PW@H-KAF) with a high specific surface area (326-353 m²/g) with intelligent phase change was obtained. The resulting material has unique characteristics: latent heat (135.1–172 J/g), thermocyclic stability and mechanical properties (tensile strength of 30 MPa, deformation of 30%) that meet the requirements of daily use. Phase-transition fibers with low bending stiffness at room temperature can be woven into threads and fabrics undergoing bending and folding. High resistance to washing and excellent temperature control allows it to be used in fabrics with intelligent temperature

control. Moreover, the flexural stiffness of the fibers can be significantly reduced as a result of the phase transition with increasing temperature and vice versa. This property can be used to create intelligent technical systems with shape memory.

The listed materials are far from limiting the list of composite materials that are used or have prospects for use in aircraft and rocket manufacturing. In Table 1 lists some new materials with unique physical and mechanical properties, among which is the synthetic polymer material Zylon, the tensile strength of which (in the form of threads) is 5.8 GPa [11], which is 1.6 times greater than that of Kevlar. In terms of tensile strength, Zylon threads are almost twice as strong as steel and five times lighter [12].

Table 1. Mechanical properties of high strength fibers.

Material	Tensile strength, MPa	Density, g/cm ³	Specific strength, kN·m/kg	Breaking length, km
Zylon	5800	1.54	3766	384
Fiberglass	3400	2.60	1307	133
Vectran	2900	1.40	2071	211
Kevlar49	3000	1.44	2083	212
Carbon fiber (AS4)	4300	1.75	2457	250
UHMW PE fiber	3600	0.97	3711	378

It should also be noted that some of the imide and aramid polymers can be used in the manufacture of nanofibers having a smooth surface and a diameter uniform along the entire length of the nanofiber. These materials have the necessary strength and elasticity to create polyimide or polyamide fibers from which threads and cables of various weaving are made.

A thermogravimetric study combined with DSC (STA) was carried out [13], which demonstrated the high thermal stability of the obtained samples of polyimide materials. It has been shown by IR spectroscopy that neither thermolysis nor UV irradiation of the material with different wavelengths has any effect on the molecular structure of the polyimide material.

Obtaining polymeric materials with amide fragments or a different structure is necessary for the selection and creation of a base of materials, on the basis of which it is possible in the future to create a high-strength cable for ground-space applications.

Zylon, synthesized in the last century [14], still remains one of the strongest materials with high heat resistance. Table 1 shows the mechanical properties of ToyoboZylon® AS Poly(p-phenylene-2,6-benzobisoxazole) fiber [15]. The polymer is used both in pure form and as part of composites. The introduction of Zylon into the composition of composite materials leads not only to an increase in mechanical strength, but also to an increase in the thermal stability of composites [16, 17].

The tensile strength of polymers is one of their most important characteristics. The values of the specific strength of materials are especially important for the aircraft industry, rocket science, and space technology. Specific strength is of fundamental importance when choosing materials for large space tether systems, in particular, space elevator cables.

It should be noted that usually high specific strength is a recognized factor in the weight perfection of the design. In this case, an increase in specific strength by reducing the density of the material is also important for the reason that all loads on the cable are inertial or gravitational, proportional to the mass. Therefore, an increase in the specific strength of the material not only increases the bearing capacity, but also simultaneously reduces external loads. As can be seen, this criterion can also be given a dynamic interpretation in "frequency" language. It should be noted that the Spaceward Foundation, paying tribute to the merits of Yu. N. Artsutanov [5] in promoting the idea of a space elevator, proposed to introduce a unit of material efficiency – the ratio of breaking stress (time resistance) to the

density of the material: $Yuri = \sigma_b / \rho$. This ratio, known as specific strength, is widely used in engineering. In relation to the space elevator, it would be more correct to assign the name Yuri to the dimensionless parameter $\lambda_a = \Omega r_0 / a$. This parameter relates the properties of the material to the angular velocity of the Earth's rotation Ω , which determines the loads on that particular structure; $a = \sqrt{\sigma / \rho}$ – speed of transverse waves in the cable; $r_0 = \sqrt[3]{\gamma M_E / \Omega^2} \approx 42000 \text{ km}$ – geostationary orbit radius; M_E – Earth mass; $\Omega r_0 \approx 3000 \text{ m/s}$ – linear velocity in geostationary orbit, which is comparable to the velocity of elastic waves even in existing materials.

2 Quantum-chemical simulation

The tensile strength of polymers is one of their most important characteristics. The values of the specific strength of materials are especially important for the aircraft industry, rocket science, and space technology. Specific strength is of fundamental importance when choosing materials for large space tether systems, in particular space elevator cables.

In addition to the experimental measurement of strength on tensile machines, which requires the availability of an appropriate sample, there are methods for predicting it. The most promising method seems to be one based on quantum chemical calculations. This method is based on modeling the process of polymer stretching by virtual deformation of the polymer model with energy optimization of the stretched structure [18]. Virtual stretching is performed until a state is reached when, as a result of structure optimization, its integrity is violated. The tensile strength is estimated as a result of optimization of the molecular structure, which provides a minimum of tensile energy.

To move from the strength of a single polymer fiber to the strength of a macro-sized sample, it is necessary to determine the variants of the structure of the threads and their mutual spatial stacking. Previously, computer simulation was used to simulate the stacking of Zylon chains [19]. The authors built a model using the structural formula of the minimal Zylon fragment (Fig. 1):

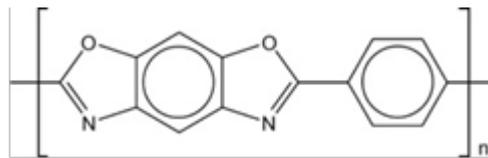


Fig. 1. Structural formula of Zylon.

Authors optimized created a Zylon model by the molecular mechanics method with the Dreiding II force field [20]. Calculations showed that this polymer forms a strictly linear monotonic chain, and the benzobisoxazole fragments are located strictly with oxygen atoms on one and nitrogen atoms on the other side of the chain. It should be noted that in a number of computer modeling methods: molecular mechanics, semi-empirical methods and abinitio methods, molecular mechanics is the least accurate method. The structure of the model of the benzobisoxazole chain fragment was calculated [21] in the popular B3LYP/6-31G(d) basis set. The fragment geometry was energy optimized, and the desired electron density distribution was obtained. The authors did not discuss geometry, but fig. 2 in the article clearly shows that the bonds of oxazole rings with phenylene rings are not parallel.

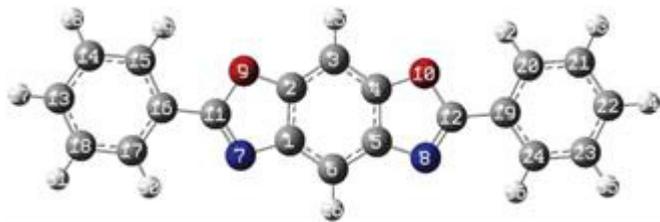


Fig. 2. Model used for calculations by K.Hu et al. The non-parallelism of the bonds C16-C11 and C12-C19 is visible.

3 Methods of calculation

In this work, we used quantum-chemical modelling using a semi-empirical method with the AM1 parameterization. The Gaussian 03 program was used for calculations. The parameterization AM1 was specially developed to calculate the energies of conformational transitions [22]. The most accurate calculation by the semi-empirical method predicts differences in the energies of various conformational states, but not their absolute values.

4 Results and discussion

A molecular model similar to that of K. Tashiro is shown in Fig. 3. The structure models a single polymer chain without contacts with its own kind, which is realized in composites with a low content of Zylon in solution.

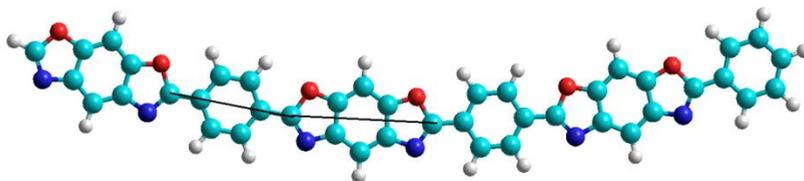


Fig. 3. Molecular model of the Zylon polymer.

The structure was energy optimized. It turned out that the structure is not straight. The angle indicated in the figure is 173° .

Calculations show that, when about 25 such fragments are formed, the chain is practically closed into a ring with a diameter of about 100 \AA . For clarity, a longer fragment is shown in Fig. 4.

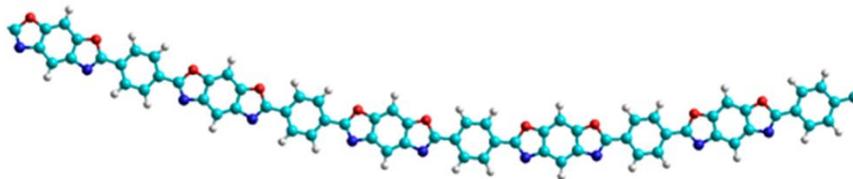


Fig. 4. Model of a long fragment of the Zylon polymer.

It should be noted that, based on general considerations of the symmetry of the carboxyl component of the reaction, there is no reason to believe that the synthesis results in a polymer with the arrangement of nitrogen strictly on one side and oxygen on the other side of the polymer chain. Fig. 5 shows two options for the location of the fragments. With a

random arrangement of these fragments in a chain, the latter will be a broken line, consisting of segments of arcs of different lengths.

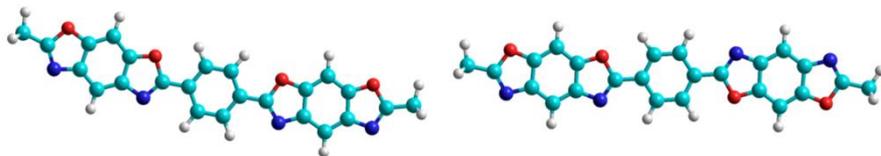


Fig. 5. Options for the arrangement of benzobisoxazole chain fragments relative to each other.

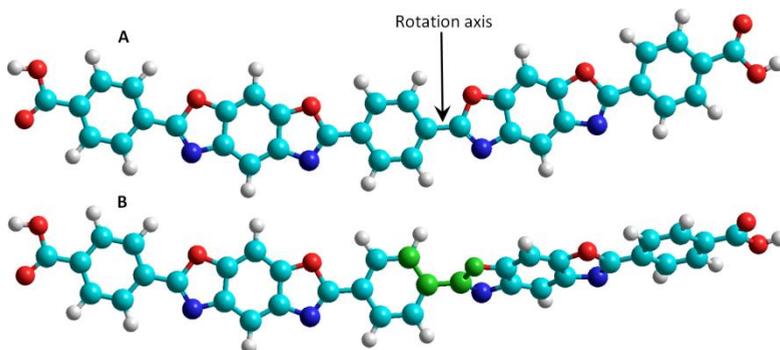


Fig. 6. Model structure used to calculate the energy barrier for rotation around the phenylene-oxazole bond; dihedral angle A - 0° , B - 60° ; atoms forming a dihedral angle are highlighted in green.

To determine the rotation barrier, in addition to calculating the minimum energy of the model shown in Fig. 6A, the energies were calculated for states with a forced dihedral angle on the bond between the phenylene and oxazole rings. The connection around which the rotation was performed is indicated by an arrow in Fig. 6. As an example, Fig. 6B shows a view of the same structure but with 60° . The difference in energy between the 0° dihedral state and the forced state is shown in Fig. 7.

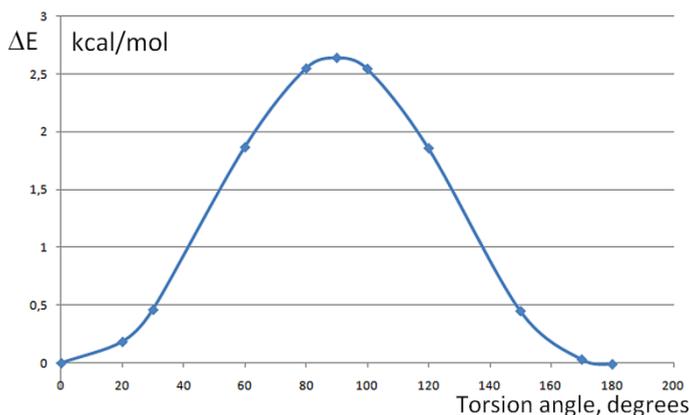


Fig. 7. Change in the energy of the model structure during rotation around the phenylene-oxazole bond.

The points correspond to the calculated energy values. The difference in energies for dihedral angles of 0° and 90° was 2.63 kcal/mol, which corresponds to free rotation. It is clear that under normal conditions in a polymer in the form of a block, rotation will be very difficult due to contacts with adjacent chains, but during the synthesis (and the

polycondensation reaction is carried out in a solution in polyphosphoric acid at temperatures up to 190°C), rotation at the growing ends of the chain will undoubtedly be. And as a result of processing a polymer array into a thread by drawing from a hot solution or melt, rotation around some bonds similar to those indicated in the figure is possible.

Rotation along the axis indicated in Fig. 6 by 180° leads to an alternative conformer. We will denote the conformer in which the nitrogen atoms in the nearest oxazolone fragments are on the same side as cis conformation, and the conformer in which the nitrogen atoms in the nearest oxazolone fragments are on opposite sides as trans.

Consider a section of a polymer chain with a length of six monomer units. There are five axes of rotation between the monomeric units in this section. Accordingly, there are 32 conformational variants, of which 8 are unique, and the remaining 24 make up 12 pairs of identical structures. In these pairs, one sequence of cis-trans conformers is identical to the other when read in reverse order. The range of chain lengths consisting of six fragments is from 71.5 to 73.1 Å. The average length for all variants is 72.7 Å. Thus, the chain length per one monomeric fragment is ~12.1 Å.

5 Conclusion

The Zilon chain is not strictly linear, but is a broken line. The benzobisoxazole units included in the chain are oriented by nitrogen atoms both in one direction and in the other. Multidirectional orientation arises in the process of synthesis. The rotation barrier of the benzobisoxazole block is low, and if the rotation is not impeded by densely spaced neighboring chains (dilute low-viscosity solution, elevated temperature), then when mechanical loads are applied, corresponding conformational transitions of polymer chains are possible. The length of short segments weakly depends on their conformational composition. However, long chains that include large loops will stretch when external forces are applied, which can lead to an increase in the size of the molecule along the stretching axis and, as a result, to a noticeable elongation of the fibers in the composition of the threads during their stretching with the limiting distance between the ends determined by the degree of polymerization and specific with a length value of 12.1 Å per monomeric unit.

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