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Polymer matrix nanocomposites from the ecological aspect in the automotive industry

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Abstract. Meeting the stringent requirements of the automotive industry that the material must meet in terms of price and performance is a serious challenge for engineers. The use of lightweight materials has led to the use of polymer nanocomposites in the automotive industry but has also led to new issues such as the impact on the ecological aspect of the environment. Tests, which are still ongoing, have found improvements in many material properties such as mechanical, thermal, electrical, optical and magnetic. So, on one hand, improved properties and low prices of production and manufacturing have been recorded, on the other hand, there is insufficient research of their impact on the environment, which this paper aims to investigate.

1. Introduction

Over the last few decades, the automotive industry has made great effort in the development of lightweight parts using innovative and easy-to-process materials, i.e. nanocomposites. Nanocomposites, regardless of the type of matrix (metal, polymer and ceramic) and the type of nanofiller, have attracted huge interest from researchers due to their potential for various applications.

Nanocomposites with a polymer base (Polymer Matrix Nanocomposites, PMNC) are materials that represent a new generation of materials with improved physical, mechanical, thermal, electrical, magnetic and optical properties. The improvement of the mentioned properties of PMNCs depends on the development of a practical and economical composition (combination of various matrices and nanofillers), as well as methods for the production of materials at the nanoscale level. Great progress has been made in meeting this challenge, which can be seen in the development of a wide range of production processes, products and devices. PMNCs are non-toxic and biostable, so they can most often be found in the military, automotive industry, space industry, construction, but also in the medical industry and cosmetics. These materials have gained great interest of the automotive industry because of their outstanding performance that enables cost reduction, weight reduction, and product improvement [1-3]. Most commonly used polymers, as a matrix for PMNCs, are polyamides, which represent a very important class of polymers.

Polyamide 6 is a thermoplastic material used in a variety of industrial applications due to its impressive mechanical and thermal properties, good processability, chemical and abrasion resistance, and biocompatibility. In the automotive industry, polyamides are used in a wide range of applications such as fuel tanks, reservoirs, pipes, pipelines, carburetors, injectors and electrical distributors [1].



Testing of the mechanical characteristics of nanocomposites with a polymer matrix and different types of nanofillers has been carried out by many researchers who have proven improvements in properties, in comparison to the basic polymer matrix [3-5]. By applying a full factorial design of the experiment, Mozaffari et al. have optimized the content of carbon nanotubes in polyamide 6/polyolefin elastomer (PA6/POE) blends, in order to improve mechanical properties of nanocomposites. They conducted tensile and impact tests and concluded that the addition of 2 wt% of carbon nanotubes has improved the tensile strength, elastic modulus, and impact strength. Through SEM analysis (Scanning electron microscope, SEM) of the tested materials, they found that the appropriate distribution of carbon nanotubes in both polyamide matrices was achieved, which resulted in the improvement of the mentioned properties [4].

By researching polymer nanocomposites based on PA610 and reinforced by graphene nanoplatelet (GNP) Kiziltas et al. have shown that it is possible to use GNPs to improve the mechanical and thermal properties of PA610. The resulting nanocomposite is suitable for the production of automotive parts [1].

Research carried out by Dabees et al. showed complementary improved performance of melt-extruded polymer nanocomposites reinforced with multi-walled carbon nanotubes (MWCNT) and TiO₂ particles, in addition to awareness of their mechanical properties. The new hybrid nanocomposite had properties in form of tensile strength increased to 82 MPa, as well as positive hardening effects. The higher crystalline properties of the hybrid nanocomposite improved the mechanical properties of the nanocomposite. The synthesis of TiO₂ and MWCNT leads to the improvement of the flame resistance characteristics of the polymeric material PA6, which has a synergistic effect [6].

A review of polymer nanocomposites with graphene as nanofiller was performed by Madhad and Vasava. They found that, with a low content of graphene in the polymer, it is possible to produce a material with higher performances, in comparison to other polymer nanocomposites. By reviewing the literature, they found that the mentioned material gained a lot of attention of scientists, due to the possibility of achieving improvements in properties, such as electrical, mechanical, thermal, flame retardant, and gas barrier, by carefully selecting the synthesis technique for graphene polyamide (G-PA) nanocomposites. They found that the method of preparation of these materials depends on their potential application, as well as that a combined approach in production that is environmentally friendly has been occurring in recent years, and great improvements in material properties have been achieved, which indicates that G-PA nanocomposites are materials for future innovations [7].

Numerous scientists, engineers and technologists constantly invest a lot of their time and energy in research, in order to create a suitable final product for a specific application. Although scientific knowledge and engineering development of these materials are joint, which is proven by a large number of published scientific works and books on PMNCs, there is still a great need to pay even more attention to protection of environment during and after the usage of these materials. Therefore, in the last few years, research has been directed towards biopolymer nanocomposites.

The aim of this paper is to research the impact that PMNCs have on the environment, by reviewing the results of application of these materials in the automotive industry, given that the expansion of the application of these materials is predicted in the future.

2. Polymer Matrix Nanocomposites

Polymer nanocomposites are materials with a polymer matrix and nano-sized reinforcement. The properties of polymer nanocomposites depend on the type of matrix, type, size, shape and concentration of nanofiller particles and the interactions between the matrix and the nanofiller. Improvements in the properties of nanocomposites, especially mechanical and thermal, are evident, compared to both materials individually, as well as polymer composites. During the process of production of the material, the dispersion of the nanofillers in the polymer matrix must be taken into account, because the said improvements are achieved through their homogeneous distribution [8]. It is generally known that the research, testing and application of nanocomposites depends on the needs and requirements of the industry.

Polymer nanocomposites have variety of applications in various industries, especially in the automotive and packaging industries. Also, another application of polymer nanocomposites, related to the production and storage of energy through the improvement of existing energy devices and the creation of new smart energy devices, was registered. Modern constructions and vehicle components for the automotive sector require the development of new robust and light materials, which indicates that it is a sector of the economy that is developing very quickly [9, 10].

In the production of polymer nanocomposites, different synthesis methods and different fillers are used. The distribution of filler particles in the polymer matrix depends on the method of obtaining the composite. Three most applicable methods for obtaining these materials can be singled out, namely: in-situ polymerization, solvent mixing and melt mixing. The oldest and simplest method, when there is no chemical bond between the polymer matrix and filler particles and when the polymer matrix is a thermoplastic polymer, is mixing nanoparticles in polymer matrix. Regardless of the mixing method and whether or not the surface modification of the nanofiller particles has been performed, it is difficult to achieve a homogeneous distribution of the nanofiller particles and prevent their agglomeration in the polymer matrix, by mixing. The method of mixing nanoparticles into a polymer solvent is used for nanocomposites with a polymer matrix, which contain silicate sheets, using a solvent in which the polymer is soluble, and in which the silicates have the ability to swell. The melt mixing method is performed by mixing the components, using the temperature to initiate the polymerization (most often the annealing process), where the polymer and the layered base are heated to the point of polymer softening [11].

A more homogeneous distribution of particles can be achieved with polymer nanocomposites that are obtained by synthesis of a polymer matrix in the presence of nanofiller particles (in-situ polymerization) or by in-situ synthesis of nanofiller particles in a ready-made polymer base. This method of polymerization is performed by heating, using a catalyst or exposing the nanosheets to radiation [11]. Many types of different polymers are used as a matrix for polymer nanocomposites, such as nylon, polyester, polypropylene or teflon, also inorganic components such as nanoparticles, nanoclay and carbon nanomaterials are integrated with said polymer matrices. This aims to form polymer nanocomposites with the required properties, which depend on the combination of components [11, 12].

Environmental issues and rising fuel costs are now causes of concern for buyers, sellers and manufacturers in the automotive industry. PMNCs are seen as one of the means to solve the following issues: improving fuel efficiency, reducing production costs and reducing greenhouse effect gases emission. The mentioned issues have become the primary goals for the automotive industry.

3. Consequences of the application of polymer nanocomposites in the automotive industry

PMNCs are materials that have attracted attention of researchers worldwide due to their potential for various applications, such as fuel economy, pollution control, energy storage, transportation and security, sensing and actuation, electromagnetic absorption, etc. In this part of the paper, the results of the research of PMNCs that are being used in the automotive industry, will be presented and analyzed, with reference to the results of their impact on the environment.

The first car part made of polymer nanocomposite was recorded in 1991. So, first the cover of the timing belt transmission was made for the Toyota Camry, and then the application of PMNCs was also recorded for other parts of the car, such as: engine cover, fuel hoses, fuel valves, door frames, seat backs, etc. The use of lightweight materials for the production of automotive components affects the reduction of vehicle weight, which causes a reduction in fuel consumption, and therefore reduction in the emission of harmful gases. PMNCs reinforced with carbon fibers are materials of which a share of about 50% of parts of a Boeing 787 and of the Airbus A380 are made. PMNCs reinforced with glass, carbon or aramid fibers can also be used for construction of ships and other means of transport [2, 13-15].

PMNCs are used in various parts of automobiles, for example, in engines, drive systems, braking systems, exhaust systems, catalytic converters, body and frame parts, paint and coatings, lubrication, tires, and electrical and electronic equipment [2]. This applications are shown in the Figure 1.

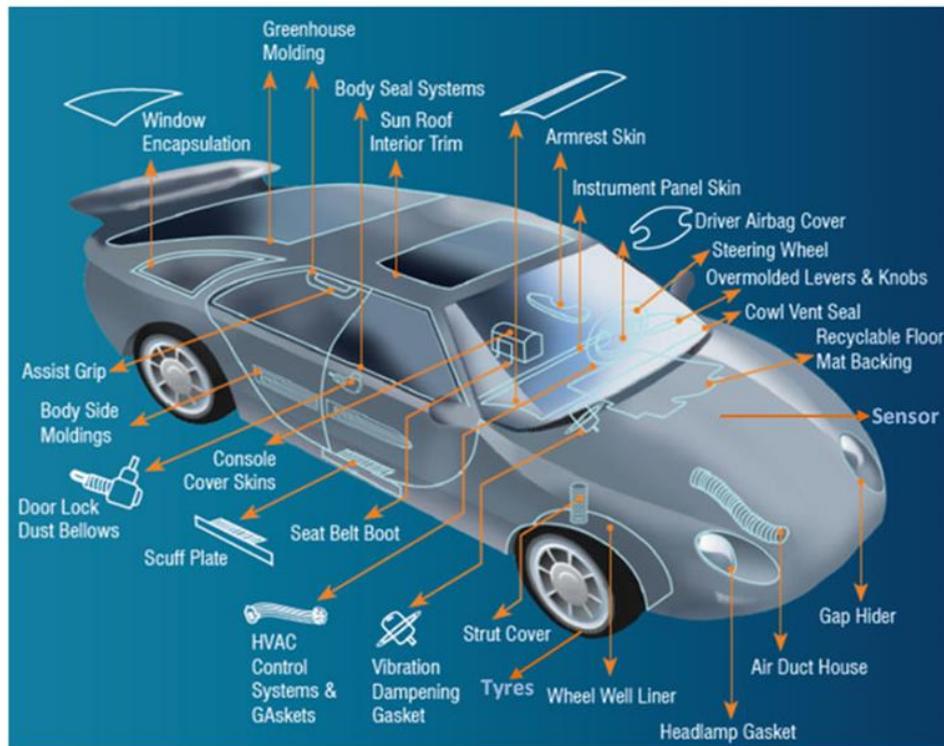


Figure 1. Potential applications of polymer nanocomposites in the automotive industry [16].

In applications of polyamide clay for parts "under the hood", the modulus and heat dissipation temperature increase, without the loss in elongation. Studies by researchers from Toyota have shown that the application of this polymer nanocomposite, at room temperature, reduces the water permeability of the nanocomposite by 40%, the tensile modulus increases by 168%, and the thermal distortion temperature by 87°C, compared to unmodified polyamide-6. These properties occur due to the large volume of polymer chains, which are limited by their interaction with exfoliated clay lamellae [17].

Multiwalled carbon nanotubes have been used commercially as a conductive additive for plastics since the 1990s. In fuel lines, these nanotubes improve conductivity, but also allow preservation of barrier properties, which is an advantage in sense of seams and gaskets. Other possibilities of application of multiwalled carbon nanotubes include application in automotive electronics, where they have the advantage of minimal peeling and the possibility of electrostatic painting, in exterior body panels [17, 18].

Different types of nanoparticles, such as nanoclay, carbon black or graphene, are dispersed in coatings and then sprayed on the surface of the car, in order to prevent external influences on organic coatings. These inclusions increase stiffness of coating, wear resistance and self-cleaning ability of the coated component. The mechanical properties of liquid lubricants can be improved by adding nanoparticles, which results in improvements in the form of reduction of friction and oil consumption, reduction of fuel consumption, increase of lifetime and performance of engines, as well as doubling the lifetime of engine oil [18].

Polymer nanocomposites have also found their application in the production of car tires, where they are used to improve safety, fuel efficiency and steering control. Motor vehicle tires contain materials such as carbon black, nanoclay, carbon nanotubes and graphene, as well as oils and other additives, surrounded by a matrix of polybutadiene and styrene-butadiene rubber. By dispersing carbon black in the nanoscale, an increase in the tensile strength of the rubber is achieved, as well as resistance to wear. Also, silicon dioxide nanoparticles can significantly improve rolling resistance in comparison to other additives, so they are used to increase rolling resistance and wet traction [18].

When talking about reducing fuel consumption, the emphasis is on reducing the weight of the vehicle, which can be achieved by using lightweight materials. Reducing the weight of the vehicle results in a reduction in the emission of gases that pollute the environment, as well as an improvement in the performance of the vehicle. A significant reduction in vehicle weight is achieved by reducing the dimensions of the engine itself, which is most quickly achieved by eliminating the need for engine fairings. By applying biopolymer nanocomposite materials, a significant reduction in the weight of the engine can be achieved, which results in a reduction of fuel consumption by about 7%, which is a very important achievement, if the long-term results are being considered [17].

It is predicted that renewable energy sources will come to the fore, in terms of solving the problem of energy shortages and environmental problems caused by the use of fossil fuels. In recent years, efficient energy management requires energy storage, which is provided by an electrochemical system composed of batteries, fuel cells and electrochemical capacitors. In particular, supercapacitors and batteries have attracted the attention of researchers, as an alternative to classical energy storage systems [29]. As it is well known, electric vehicles are one of the most popular ecologically friendly solutions. On one hand, they do not use chemical fuels, but electricity to charge their batteries. On the other hand, the batteries they use have low capacity [19].

Supercapacitors are energy storage elements with significantly higher energy density than conventional capacitors and batteries. The use of supercapacitors ranges from plug-in hybrid electric vehicles to backup power sources. Effective use of supercapacitors implies new, improved, but also more economical, environmentally friendly materials for electrodes [20].

Currently, several polymer nanocomposites meet the requirements in terms of production volume, environmentally acceptable and superior mechanical properties, better operating temperature, good surface finish and improved corrosion resistance and are considered as potential materials for structurally non-critical parts, such as front and rear fascia, bonnet, ventilation grill and valve covers. The use of polymer nanocomposites in these parts could result in a weight reduction of several billion kilograms per year [21]. More about the application of polymer nanocomposites in the production of car parts can be found in the literature [2].

According to previous research, in order to achieve the simplest and greatest commercialization of PMNCs, it is necessary to emphasize the development of fast and cheap analytical methods for small samples, which can provide a certain degree of exfoliation and orientation, because rheology, and similar methods, require too much time and money [22].

The impact of nanomaterials have on the environment and human health has not yet been sufficiently investigated, but what is certain is that the impact of polymer nanocomposites on the environment is different from the impact of the polymer and the nanomaterial separately [23, 24]. Environmental pollution is a global issue and has a negative impact on human development. However, with the increased use of nanomaterials, the number of researches and tests of these materials on the environmental impact increases proportionally, with the aim of preventing serious health problems that can arise, for example, from deteriorating water quality.

3.1. Biodegradable polymer nanocomposites

Some polymers have the ability to naturally biodegrade, which is very useful in reducing the impact these materials can potentially have on the environment. They break down into their constituent components over time. The issue may occur only if their components are individually toxic, which can cause more damage than the combination of nanomaterials and polymers. Small dimensions of the constituent components do not actually equal less impact, but enable them to have a better penetration ability and a thus, they become greater risk to the environment. Separation of constituent parts can occur especially if polymer nanocomposites are incinerated with waste materials [1, 23].

Biodegradable polymers are generally not durable for long-term use in extreme conditions (humidity, hot or cold environments, etc.), and therefore are not practical for applications that require long-term durability and stability. The use of bio-based polymers is increasing due to recent advances in the

development of cost-effective production technology, thereby reducing the cost and performance aspects of the material [1].

Those polymers that do not have the ability of natural biodegradability are deposited as permanent waste, which can be seen from the example of plastic that is deposited on the surface of the lake. Over time, it begins to block sunlight, causing damage to the ecosystem of the lake, and also affecting the quality of the water, thus indirectly causing damage to public health.

3.2. Green plastics

A material that is harmless to people and the environment, and at the same time economical in terms of production, is clay. However, clay does not have an unequivocal effect on the degradability of nanocomposites, because the natural degradation of clay depends on the surface substances of the clay, which are used in the modification, during the bionanocomposite production process, as well as on the nature of the specific type of clay used in production [1, 25]. In Figure 2 the life-cycle of biodegradable polymer nanocomposites is shown.

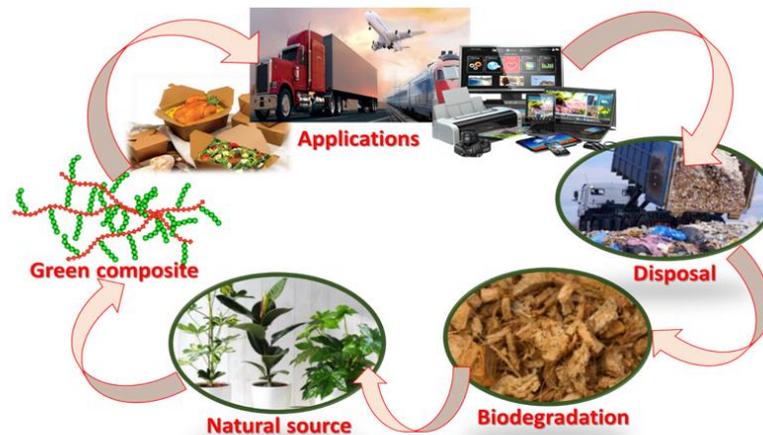


Figure 2. Application and disposal of green composites [26].

Several research efforts have been made to investigate the basic properties of PA nanocomposites containing nanoclay. According to their research and results, an improvement in thermal stability and mechanical properties of the nanocomposite was recorded, because a homogeneous dispersion of nanoclay in the PA matrix was achieved [27]. Tests in which triethyl citrate was used as a plasticizer and nanoclay with cellulose acetate, included, among other types of tests, strength testing and X-ray diffraction, and showed that it is possible to use these materials for the production of biodegradable, environmentally friendly polymer nanocomposites [23].

3.3. Standardization and nanosafety

The methods of testing the properties of polymer nanocomposite materials are similar to the methods used for simple polymers. Although there are standards for the testing of nanomaterials, within ISO and ASTM [28, 29], many of the tests it entails refer to their properties in a physical or chemical sense, rather than their toxicity. However, the nanomaterial in the polymer nanocomposite is actually a factor that can cause issues when using or disposing of the material.

Therefore, the biggest danger to the environment is not actually polymer nanocomposites, but their constituent parts and especially during the process of their disintegration. Previous research has shown that there is no possibility of complete removal from the waste gas, for material below 100 nm in size, with the exception of carbon nanotubes. Nanotubes can have a negative impact on the environment only when leaking from solid residues [23]. Tests performed on mice exposed to multi-walled carbon nanotubes (MWCNTs), a material researchers are more familiar with, showed a 90% chance of cancer

development in these animals, but there is still no solid evidence that nanocarbon is carcinogenic to humans [30].

It can be concluded that the constituent components of polymer nanocomposites will eventually end up in the environment, through waste gas or solid residues, so it is very important to determine the correct ways of disposing of these materials, not just the way of their exploitation. It has already been established that incineration of waste is not precisely a good way of disposing of polymer nanocomposites. Consequently, it is predicted that for the future needs of using these materials, it will be necessary to develop new disposal procedures, in order to ensure that these materials do not end up in the environment and thus potentially endanger it [1, 23].

The development of new graphene-based materials and their use in the automotive industry is one of the solutions to reduce the impact of future vehicles on the environment. It is necessary to create concepts of new materials with the latest safety design approaches by developing and optimizing advanced ultra-light polymer materials based on graphene, efficient compositions, production processes and life-cycle analysis. According to European requirements, 95% of a vehicle must be made of materials that can be recycled and are environmentally friendly. On that basis, the growth in the use of materials such as biofibers and bio-based resins produced from soybeans, pure cellulose acetates and citrate-based plasticizers is predicted [22].

There are many car manufacturers that actively and increasingly use biopolymer nanocomposite materials in the production of components. The most famous among them are BMW, Audi, Ford and Mercedes-Benz, which, for certain series of cars, use polymer nanocomposites based on sisal, flax, and rice husks, for making door panels, roof panels, seat backs and other components. Manufacturers such as Toyota, Honda, Nissan or Volkswagen use biopolymer nanocomposites based on sugar cane, banana or nettle in the production of floor mats, spare tire covers, interior fabrics, dashboards and radiator end tanks [10]. Manufacturers like Peugeot, Opel, Rover and Citroen, also use nature fiber-reinforced nanocomposites in production of interior and exterior door panels, rear storage panels, as well as front door panels [31].

Relatively easy method of production, unique combination of properties and low prices of polymer nanocomposite materials enable their wide range of applications and wide use in the automotive industry. Today's main goal of the automotive industry is to protect the environment and satisfy consumers by using sustainable, recycled, waste by-products and bio-based polymers. It is expected that the production of plastics will increase up to 3 times compared to the production of 10 years ago. Accordingly, the consumption of petroleum oil for the production of plastics is predicted to amount 20% of the total oil-based resources by 2050 [1]. Figure 3 shows the expected growth of the global biopolymer nanocomposite market for year 2026.

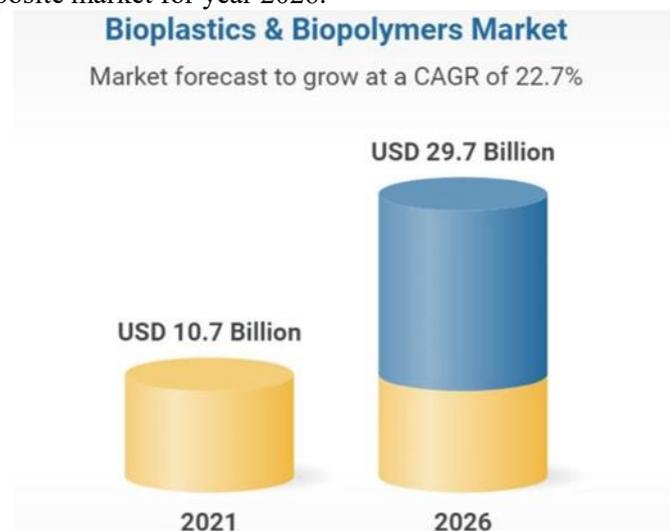


Figure 3. Market forecast for biopolymers [32].

It can be concluded that the automotive industry is investing a lot of effort in research for reduction of environmental pollution using PMNCs. Their main goal is to use an increasing number of sustainable materials, wherever possible, without compromising durability, product quality and performance.

4. Conclusion

Polymer nanocomposites have gained great interest of industry in recent years. By choosing the appropriate polymer matrix and nanofiller, it is possible to get a nanocomposite material with the required properties that none of the initial materials possess.

Based on the review of previous research, it was established that it is possible to obtain a high-quality, improved strength, ionic conductivity, biodegradability and bio-stable materials with polymer nanocomposites, compared to traditional composites. These materials are widely used in the electrical, aviation and automotive industries, as well as in food packaging, biotechnology, medicine, pharmacology, space and military technology because of their unique combination of properties, low price and a relatively easy way to acquire them.

In recent decades, the issue of environmental protection is an increasingly common topic in many spheres of industry. Ecologically acceptable solutions for production and exploitation are more appealing to both customers and producers, because, with the development of new technologies, this solutions are often proven to be cheaper and of higher quality. Some of the largest car manufacturers in the world saw the advantage of using polymer nanocomposites many decades ago, so today these materials are widely used for the production of a wide range of car parts. Tests that were performed on polymer nanocomposites were mostly related to their properties and possibilities of their exploitation, and less often related to their impact on the environment. This led to the fact that the method of disposal and degradation of these materials has not yet been studied to a sufficient extent, needed to control, and as the ultimate goal of the study, eliminate the dangers related to the impact of their degradation on the environment, and indirectly on human health.

With the continuous growth of the popularity of nanomaterials, and insufficient knowledge of their possible toxicity, it is necessary to pay great attention to the protection of personnel who are directly exposed to potentially dangerous nanomaterials, during their daily use, as well as to the protection from indirect danger that threatens with pollution of the environment.

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