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Improving the mechanical and thermal properties of polyurea by adding nano-aluminum oxide

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Abstract

This study utilized polyurea as the core material and nano-aluminum oxide as the reinforcement material at varying weight percentages (0.5%, 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, and 9%) to produce a composite material. Mechanical tests (hardness, tensile strength) and thermal conductivity were then performed on the specimens. The tests revealed that reinforcing the polyurea with nano-aluminum oxide enhanced its mechanical properties, resulting in a 10% increase in hardness and tensile strength compared to the base material. Thermal properties, such as thermal conductivity at room temperature, also increased after heat treatment of the material following the addition of nano-aluminum oxide reinforcement at temperatures of 7 and 80°C. The best result was obtained at a weight percentage of 1%.

Keywords: Polyurea, nano-aluminum oxide, hardness, tensile strength, thermal conductivity.

Introduction:

Researchers have focused their attention, due to scientific and technological progress [1], on the subject of manufacturing composite materials, which are materials resulting from the combination of two or more distinct materials, each representing an independent phase in the system. This is aimed at obtaining new materials with properties suitable for industrial applications [2,3]. Mechanical properties vary depending on the type of supporting material added, as we find that the effect of supporting materials may be limited to improving some properties of composite materials without others. For example, we find that adding graphite and phosphorus to polyurethane as reinforcing materials improves the thermal properties of these materials without affecting their mechanical properties [4]. We also find that some researchers have studied the compressive mechanical properties of polyurea at a limited range of strain rates [5,6]. Yi et al. studied the behavior of a single polyurea sample and three polyurethane samples under compressive force using a Hopkinson-Son compression test, revealing a nonlinear stress-strain relationship that is significantly affected by the strain rate [7]. Sarva et al. also studied. The behavior of polyurea and polyurethane at various strain rates was investigated using various testing methods, including a screw-driven mechanical test, indicating rate dependence [8].

Additionally, Zhang et al. investigated the stress-strain behavior of two polyaspartic acid polyurea esters at strain rates ranging from 0.001 s^{-1} to 1500 s^{-1}. However, limited research has been reported on the failure and damage mechanisms of polyurea under dynamic loading [6]. Recently, nano-reinforced composites have attracted the attention of many researchers in an effort to improve their mechanical performance [9]. Therefore, to enhance the properties of polyurea, some researchers have added nanoparticles to polyurea to improve its mechanical properties. In these studies, several nano-reinforced materials, including multi-walled carbon nanotubes and nanoclay, have been incorporated into the composites, and their mechanical behavior has been investigated under low strain rates [10,11]. With the development of polymers, a number of polymeric materials have been widely used to improve the protective performance against explosions and ballistic shocks [12,13]. This can be attributed to polymeric materials possessing excellent properties, such as high specific strength, lightweight, and low cost.

Polyurea is a flexible polymeric material produced in the form of a chemical reaction between an amine component and an isocyanate component [14,15], which can improve the survival of structures under explosion conditions and intense shock load [16]. For protective structures, polyurea is widely used as a coating in the outer or inner layer of composite structures [17,18] such as vehicles, ships, and buildings [5]. Therefore, it is necessary to investigate the mechanical properties and failure mechanisms of polyurea materials at various stress rates.

Polyurea exhibits elastic properties because it consists of polymer chains linked in a network structure, which gives it a high level of elasticity [7,19]. It is a chemically cross-linked random polymer with a phase-separated microstructure comprising both hard and soft components, resulting from thermodynamic incompatibility [20,21]. Originally used in ballistic systems and devices for its energy absorption, polyurea has numerous applications in the construction field. It is commonly used as a waterproofing coating for industrial floors and as a reinforcing coating for steel and concrete. Composite materials are classified based on the matrix into polymer-based, mineral-based, and ceramic-based composites [22]. Polyurea is formed by the reaction of diamines with diisocyanates, as shown in the following equation:

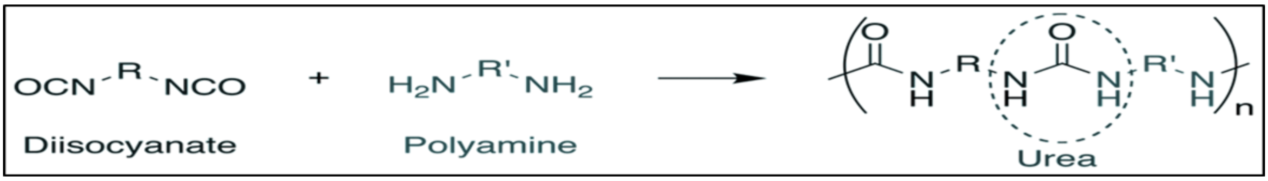

Fig. 1. Chemical formation reactions of polyurea, depending on the alkyl groups R, R

There are several methods that can be followed to prepare polyurea, which is the result of the reaction of two materials, each containing at least two active groups. One of these methods is spray coating. Spray coating is used to protect concrete structures from corrosion in construction, as well as in cars and marine vessels, due to its durability and rapid hardening [23]. However, polyurea coating has disadvantages, including its higher cost than traditional coatings, the requirement of special tools and trained workers, and a short pot life. Polyurea coatings dry quickly, which is beneficial in some aspects, but it can also be a problem because they do not remain viable for long after the line is finished. This means they need to be applied quickly and efficiently [23]. Reaction injection molding (RIM) is utilized in industry due to its large production volume and the associated expensive equipment [24]. Casting is the most widely used method for studying the various properties of polyurea, due to its low cost and the ease of its mixing processes [25]. Polyurea is divided into several types, including pure polyurea and hybrid polyurea [26].

In this study, polyurea was prepared and then reinforced with nano-aluminum oxide. Its mechanical properties, including the modulus of elasticity and hardness, as well as the thermal properties represented by thermal conductivity, were studied.

Practical Part

Materials Used in the Research

-Base Material:

A mixed ratio of diisocyanate and diamine (provided by ALCHIMICA BUILDING CHEMICALS) was used in the polyurea preparation process. 1:1 was the optimal mixing ratio for producing a flexible, durable, and low-viscosity polyurea compared to other mixing ratios.

-Reinforcing Materials:

Aluminum oxide nanoparticles were used as the supporting material, supplied by Guangzhou Hongwu Material Technology Co., Ltd., without any further purification. This material is a fine powder with a high surface area, giving it excellent adsorption and catalytic properties. Its particle size is between 20 and 30 nm, its chemical formula is Al2O3, and its molar mass is 101.96 g/mole.

Method of Work

The preparation of composite materials is one of the final and most crucial stages in the polymer industry, as it determines many of the product's characteristics, such as tensile strength, hardness, and the final shape of the polymer. It is well known that various methods can be employed in manufacturing these materials, including manual molding, which may be followed by reinforcement with nano-aluminum oxide at different weight ratios. The base material (polyurea) is placed alone, without any supporting materials, in a mold of known weight and size. After the casting process is completed, the models are left at room temperature for 24 hours to complete the hardening process and homogeneity between the particles. The process is repeated, but after adding the supporting material (nano-aluminum oxide) to the polyurea to produce the composite materials.

Equipment used to test mechanical properties

Tensile testing machine

A universal testing machine, made in China and manufactured by HONGJIN TEST INSTRUMENT, was used. The ISO-R527 standard was used to prepare the samples, which were in the form of slices. The purpose of this test was to determine the properties of the composite material under the influence of a two-way axial load.

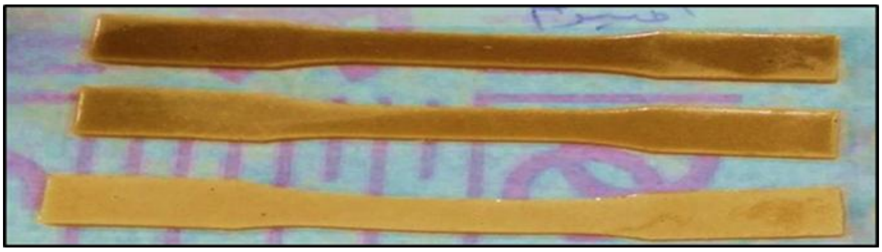

Fig. 2. Shape and dimensions of the samples prepared for tensile testing.

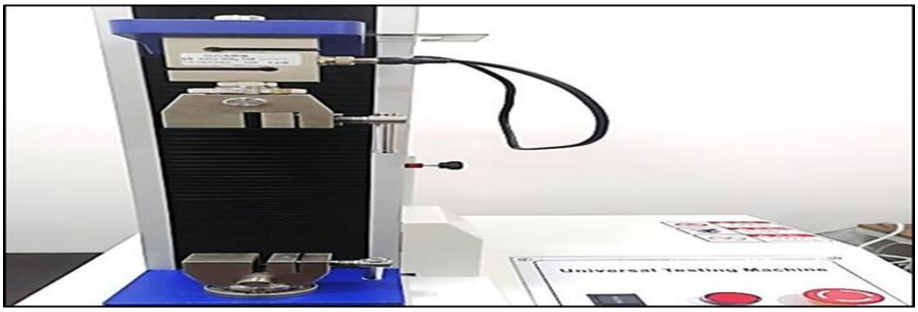

Figure (3) Tensile testing device

Hardness Tester

A compass-like device, manufactured by HONGJIN TEST INSTRUMENT, type Shore A. It features a central needle. The device is used by holding it vertically on the specimen to be hardened until the needle is embedded in the surface. The measurement is then recorded.

Fig. 4. Hardness measuring device.

Thermal Conductivity

The thermal conductivity test samples were prepared according to specifications, with a diameter of 11.23 cm and a thickness of 1 cm, which are the specifications for measurement using Lee's Disk device located in the College of Science, Department of Physics.

Fig. 5. Samples prepared for thermal conductivity testing.

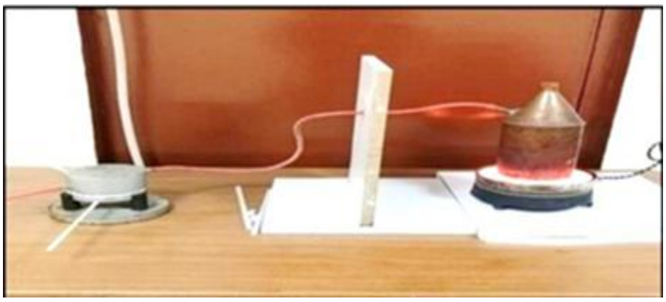

Fig. 6. Thermal conductivity testing device.

Results and Discussion:

1- Tensile Testing

This is a fundamental property of all polymers. It studies the dimensional changes in the polymer's shape as a function of stress. When a specific stress is applied to a polymer specimen at a constant, uniform speed and the resulting deformation is measured in terms of change in area, length, or volume, the polymer's behavior under stress can be identified. This can be achieved by measuring the polymer's properties in terms of strength, elasticity, the maximum stress the specimen can withstand, the maximum stretching that may occur, and other important engineering information.

Tensile strength is a measure of a material's resistance to the forces applied to it when stretched before breaking. Therefore, the intervening material is nano-aluminum oxide in the base material [27]. Table (1) and Figure (6) illustrate the increase in the elastic modulus after adding the nano-aluminum oxide reinforcement.

Table 1. Values of the elastic modulus of polyurea before and after reinforcement with nano-aluminum oxide at 25°C**.**

Compositer at 25C°	modulus of elasticity(MPa)
PUA	0.47
PUA + AlNPs 0.5%	0.51

PUA + AlNPs 1%	0.58
PUA + AlNPs 2%	0.50
PUA + AlNPs 3%	0.54
PUA + AlNPs 4%	0.56
PUA + AlNPs 5%	0.55
PUA + AlNPs 6%	0.56
PUA + AlNPs 7%	0.57
PUA + AlNPs 8%	0.55
PUA + AlNPs 9%	1.75
PUA + AlNPs 10%	0.52

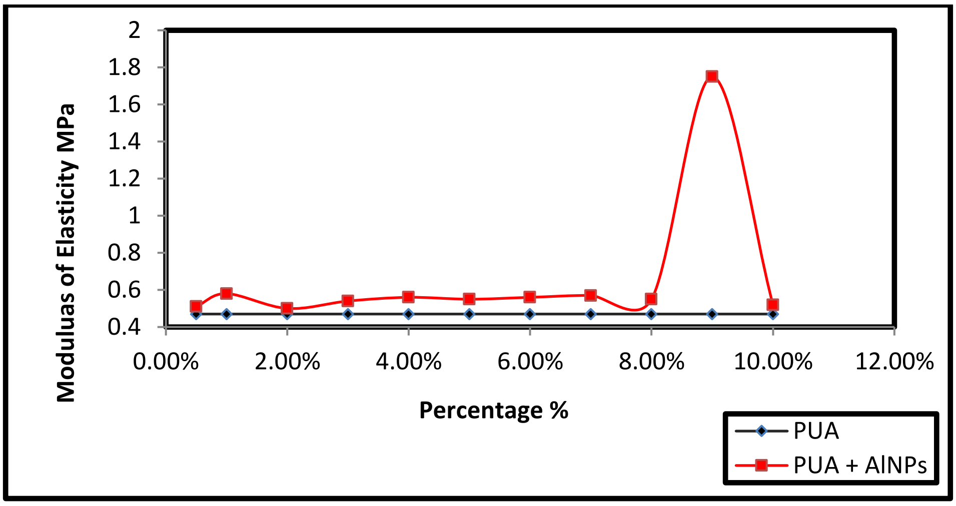

Fig. 7. The relationship between the elastic modulus and the weight percentage of polyurea before and after reinforcement with aluminum oxide nanoparticles at 25°C.

The results shown in Table (2) showed that polyurea improved after adding the supporting material nano aluminum oxide at a temperature of 25°C at a weight percentage of 1%, which reflects an increase of 23% as a result of enhancing the bonding between the nanoparticles and polyurea, which works to reduce the movement of the polymer chains and increase the resistance of the material to deformation when loaded. However, the increase in the elastic modulus value at 7°C was slight, by 6.66%, due to the restriction of the movement of the polymer chains as a result of partial freezing or relative hardening, as well as the shrinkage occurring within the structure, which leads to the convergence of the chains, and also due to the molecular effect of the nano-aluminium oxide particles. At a higher temperature of 80°C, the increase was moderate, amounting to 11.6%. At higher temperatures, elasticity increases, and the internal cohesive force between polymer chains decreases. However, when nano-aluminium oxide is added as a supporting material, it acts as a stabilizing agent that prevents this decrease. The added nano-material's structure resists thermal expansion and provides some cohesion. Here, the improvement of adding the nano-material appears more clearly than in the case of a temperature of 7°C.

Table 2. The values of the elastic modulus of polyurea before and after reinforcement with aluminum oxide nanoparticles at temperatures (7, 25, 80) C°.

Temperatures C°	Elasticity before Reinforcement	Elasticity after Reinforcement
7	0.45	0.48
25	0.47	0.58
80	0.43	0.48

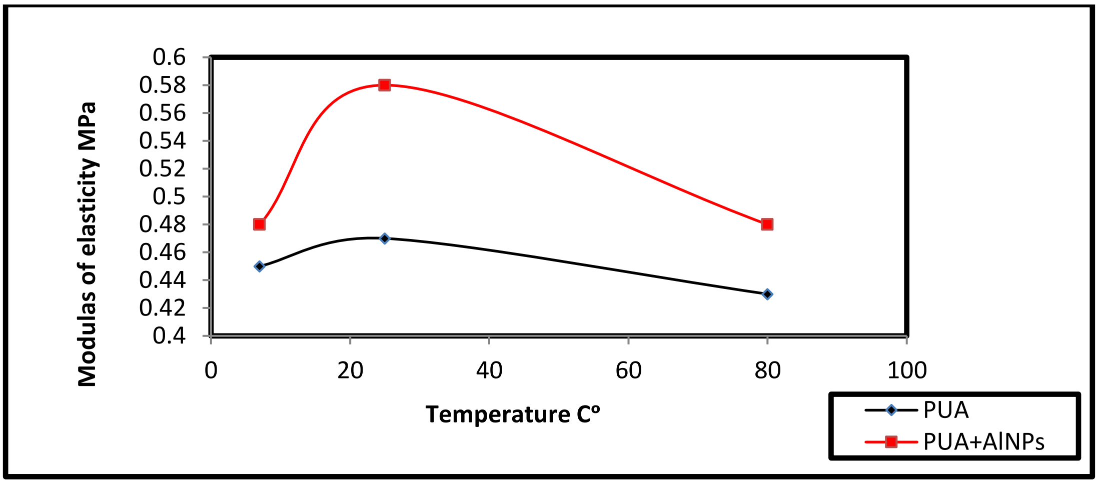

Fig.8. The relationship between the modulus of elasticity and temperature before and after reinforcement at temperatures (7, 25, 80)°C.

-Hardness test

It is used to measure a material's resistance to plastic deformation in its surface areas [28], as it is a mechanical property and a measure of plastic deformation - which a material can suffer under the influence of external stress imposed on it as a result of its general exposure to scratching and penetration by harder equipment when used in application fields [29].

Table 3. Hardness values of polyurea before and after reinforcement with nano aluminum oxide at a temperature of 25°C

Composites	Hardness resistance at 25C°
PUA	35.5
PUA + AlNPs 0.5%	52.5
PUA + AlNPs 1%	61
PUA + AlNPs 2%	56
PUA + AlNPs 3%	55
PUA + AlNPs 4%	54

PUA + AlNPs 5%	47
PUA + AlNPs 6%	41.5
PUA + AlNPs 7%	43.5
PUA + AlNPs 8%	38
PUA + AlNPs 9%	39.5
PUA + AlNPs 10%	36

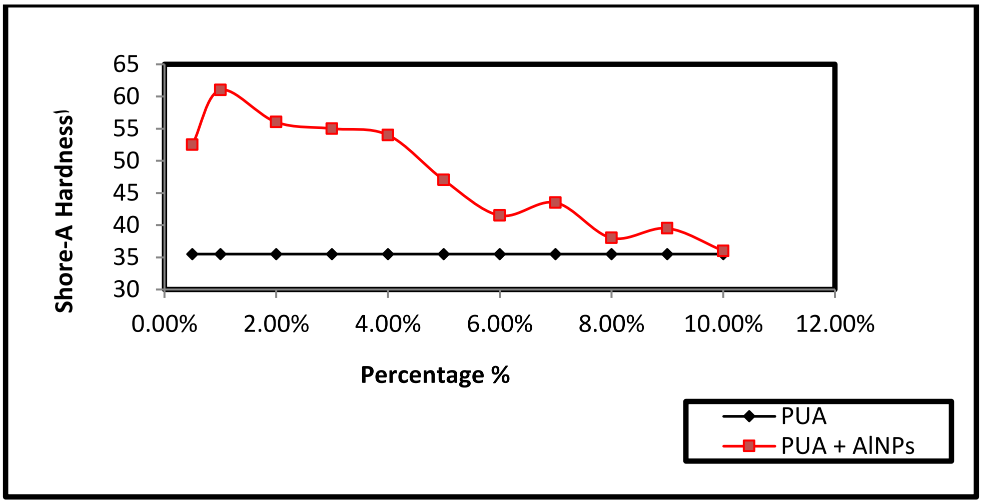

Fig. 9. The relationship between hardness values and weight percentages of polyurea before and after reinforcement with nano aluminum oxide at a temperature of 25°C.

Reinforcing polyurea with nano aluminum oxide leads to improved hardness values. The results obtained and presented in Table 3 and Figure 9 indicate that the composite material reinforced with nano aluminum oxide exhibits a higher hardness compared to polyurea before addition, due to the interlocking and intermingling between the polyurea and nano aluminum oxide [19,20]. We note from Table 3 that the highest hardness value at 1% weight percentage increased by 71.8%, and when heat treatment was carried out at temperatures (7, 25, 80 C°), we note that the hardness values increased with decreasing and increasing temperature. This increase indicates that the nano-reinforced material successfully strengthened the material structure and prevented loss of hardness at a temperature of 25 °C. At 7°C, the hardness increased as the material hardened. At 80°C, although the high temperature led to the softening of the material, the nano-aluminum oxide maintained its role in strengthening and reinforcing the structure, resulting in relative stability in hardness. These results confirm that reinforcement with nano-aluminum oxide enhanced the material's resistance to these conditions, making it more durable.

Table 4. Hardness values of polyurea before and after reinforcement with nano aluminum oxide at temperatures of 7, 25, and 80

Temperatures C°	Hardness before reinforcement	Hardness after Reinforcement

7	**44**	**58**
25	**35.5**	**61**
80	**45.5**	**57.5**

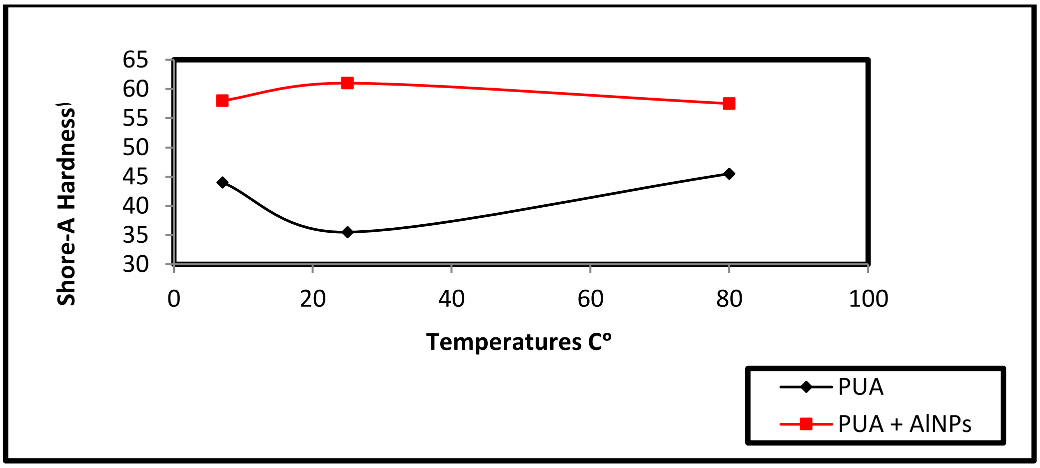

Fig. 10. Hardness of polyurea before and after reinforcement with nano aluminum oxide at .temperatures of 7, 25, and 80 °C

4-Thermal conductivity

Heat conduction is a physical property that represents a form of energy transfer. It moves from areas of high temperature to areas of low temperature in multiple forms (conduction, convection, and radiation). Heat can be transferred in more than one form, but conduction or convection is slower than radiation. This is because the speed of radiation is equal to the speed of light, 108*3 m/s, and molecules are free to move.

Table 7. Thermal conductivity values of polyurea before and after reinforcement with nano aluminum oxide at temperatures of 7, 25, and 80 °C.

Temperatures C°	**Thermal Conductivity Before Reinforcement**	**Thermal Conductivity After Reinforcement**
7	**0.0673**	**0.109**
25	**0.0764**	**0.084**
80	**0.0943**	**0.101**

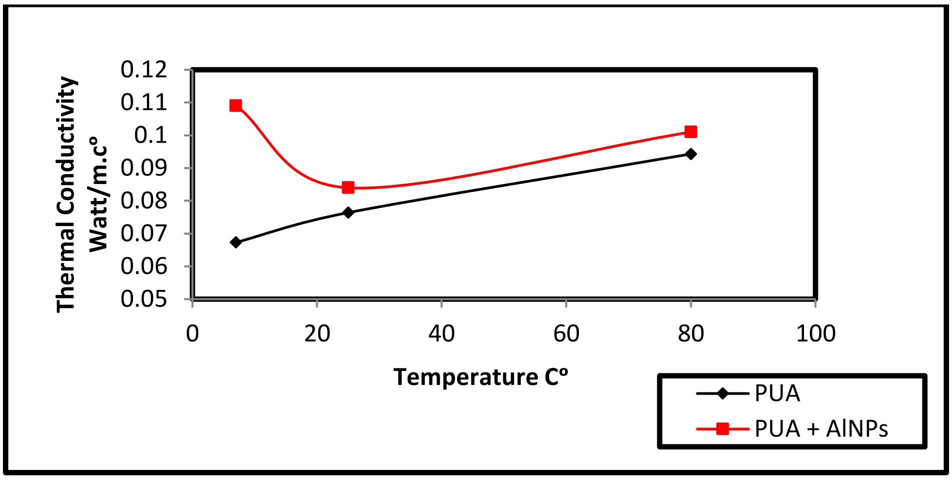

Fig. 11. The relationship between temperature and thermal conductivity.

The results in Table 7 and Figure 11 show an increase in thermal conductivity after reinforcing polyurea with nano-aluminum oxide compared to its original value at all temperatures (7, 25, and 80 °C). This improvement and increase are attributed to the nature of nano aluminum oxide, a ceramic with high thermal conductivity, which acts as a step for heat transfer within the polymer structure. The highest increase was at 7 degrees Celsius, at 62%, because the movement of the chains is limited and heat transfer depends on photons, while at two temperatures, 25 and 80 degrees Celsius, the differences decreased as a result of the movement of the chains and the increase in the scattering of photons, which reduces the efficiency of heat transfer.

Conclusions

1. The addition of nano-aluminum oxide reinforcement to polyurea increased the mechanical properties (elastic modulus, hardness.(

2. The hardness and elastic modulus increased upon heat treatment at temperatures of 7.80°C.

3. The thermal conductivity of polyurea increased after reinforcement with nano-aluminum oxide at all temperatures (7, 25, 80).

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