

ASSIS EKHLASS K. HEMADI

Department of Chemistry, Education College for Girls, University of Mosul, Mosul, Iraq

E-mail: ekhlas.22gep1@student.uomosul.edu.iq

KOSSAY K. AL-AHMADY

ORCID: 0000-0003-2771-2123

Presidency of the Mosul University, Mosul, Iraq

E-mail: prof.kossayalahmady@uomosul.edu.iq

EBTAHAG Z. SULYMAN

ORCID: 0000-0002-1798-4937

Department of Chemistry, Education College for Girls, University of Mosul, Mosul, Iraq

E-mail: ebtholim@uomosul.edu.iq

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Improving mechanical and thermal properties of unsaturated polyester resin by adding automotive glass waste

Poprawa właściwości mechanicznych i termicznych nienasyconej żywicy poliestrowej poprzez dodanie szklanych odpadów przemysłu motoryzacyjnego

The primary goal of this study was to improve a number of mechanical properties of UPE (unsaturated polyester) by using available and cheap particulate fillers, such as reinforcement with powder with a particle size of 75 μm . A composite of UPE with automotive glass waste (as filler materials) was prepared, and some mechanical and thermal properties were studied at certain weight percentages (5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, and 50%). A comparison was made between the polymeric composites before and after the process of reinforcing them with waste automotive glass, and it was found that with a 30% content of these additives they showed good mechanical properties. These additions were made at different temperatures: 8°C, 25°C and 50°C. The results before and after the reinforcement process for polymer composites showed that there was an improvement in the mechanical properties (compressive strength, hardness and impact resistance) with a decrease in the modulus of elasticity (Young's modulus). When processing was carried out at a temperature of 8°C, a decrease in the values of the mechanical properties (compressive strength, impact strength, modulus of elasticity, thermal conductivity) was observed in varying proportions, with an increase in the values of hardness. Conversely, when the samples were heated to a temperature of 50°C, there was an increase in the values of the above-mentioned properties and a significant decrease in the hardness values. Throughout the research, various measurement techniques were used, including scanning electron microscopy (SEM), infrared spectroscopy (IR) and thermogravimetric analysis (TGA). Their purpose was to monitor the changes that occurred in the polymer as a result of the use of the reinforcing material (automotive glass).

Keywords: unsaturated polyester, automotive glass waste, filler materials, mechanical properties, compressive strength, impact strength, hardness, modulus of elasticity, thermal conductivity

Głównym celem badań było poprawienie właściwości mechanicznych UPE (nienasyconego poliestru) poprzez zastosowanie dostępnych i tanich wypełniaczy cząsteczkowych, na przykład przez wzmocnienie proszkiem o wielkości cząstek wynoszącej 75 μm . Przygotowano kompozyt UPE ze szklanymi odpadami przemysłu motoryzacyjnego (jako materiałem wypełniającym) i zbadano wybrane właściwości mechaniczne i termiczne przy określonych procentach wagowych (5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45% i 50%). Porównano kompozyty polimerowe przed procesem wzmocniania odpadami szklanymi i po nim. Stwierdzono, że przy 30-procentowym udziale tych dodatków wykazywały one dobre właściwości mechaniczne. Dodatki zostały wprowadzone w różnych temperaturach: 8°C, 25°C i 50°C. Analiza wyników przed wzmocnieniem kompozytów polimerowych i po tym procesie wykazała, że nastąpiła poprawa właściwości mechanicznych (wytrzymałości na ściskanie, twardości i udarności) przy spadku modułu sprężystości (modułu Younga). Po przetworzeniu w temperaturze 8°C odnotowano spadek wartości parametrów mechanicznych (wytrzymałości na ściskanie, udarności, modułu sprężystości, przewodności cieplnej) w różnych proporcjach przy jednoczesnym wzroście twardości. Z kolei po podgrzaniu próbek do temperatury 50°C zwiększyły się wartości wymienionych właściwości i znacznie zmniejszyła twardość. W badaniach wykorzystano różne techniki pomiarowe, w tym skaningową mikroskopię elektronową (SEM), spektroskopię w podczerwieni (IR) i analizę termogravimetryczną (TGA), w celu zweryfikowania zmian zachodzących w polimerze w wyniku zastosowania materiału wzmocniającego (szklanych odpadów przemysłu motoryzacyjnego).

Słowa kluczowe: nienasycony poliester, odpady szklane przemysłu motoryzacyjnego, materiały wypełniające, właściwości mechaniczne, wytrzymałość na ściskanie, udarność, twardość, moduł sprężystości, przewodność cieplna

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1. Introduction

The second half of the twentieth century witnessed a significant expansion in the production and use of polymeric composite materials. These materials are known as a combination of two or more heterogeneous materials to produce a single material known as polymeric composites. In consequence, the resulting material has better properties than the properties of the materials that are included in its composition if each material were separate from itself. The aim of producing polymeric composites is to achieve high properties that cannot be achieved with traditional materials, such as light weight, thermal and electrical insulation, mechanical and chemical resistance, design flexibility and other qualities [1]. Composite materials depend on the shape and size of the molecules added and how they are distributed in the base material, as well as the nature of the bond between the molecules and the base material, all of which affect the properties of the final layer of the composite material [2].

The size of the global composites market was \$19.6 billion in 2011 and is estimated to reach approximately \$34.1 billion by 2018. This represents a compound annual growth rate in the use of composites of approximately 10.5% [3]. Unsaturated polyester is classified as a thermoset polymer and is the most widely used material in the world [4]. More than two million tonnes of these materials are used annually in structural products such as tanks and pipes, automotive parts such as car bodies, boat hulls and aircraft panels, and other industries [5].

To improve the strength and hardness of the polymer, fillers, or reinforcing materials, are added [6]. Reinforcing materials are of several types, including organic or inorganic, and recently a great deal of focus has been placed on organic reinforcing materials due to their low cost, relative availability and cheap price compared to the base material [4]. Glass waste is a growing burden, so there is an urgent need for new ideas to deal with these large quantities of different types of glass, including mixed, broken and contaminated glass, which currently cannot be recycled. Conventional glass recycling techniques are very sensitive and often limited by the need to separate waste glass into different types. One of the most common composites is glass fibre and glass powder, where the glass fibre or powder is embedded in a polymeric material [7]. These glass fibre reinforced polymeric materials are increasingly used as materials for bearings, pulleys, seals, gears, wheels, clutches, etc. Glass powder is often added to polymers to improve tensile strength, compressive strength, hardness, corrosion resistance, durability, thermal stability and other properties. These low-cost materials replace some amounts of polymer, which is considered relatively expensive compared to glass powder or even glass fibre, which ultimately results in a lower cost of the final product [7].

Shayan and Xu [8] stated that recycled glass waste in Portland cement and concrete has received a lot of attention all over the world due to the increased cost of disposal of cement and concrete waste and environmental concerns as a result of the accumulation of these materials, which causes harm to the environment.

The researchers [9, 10] recorded that waste glass can be effectively used in concrete as glass aggregate and is used in various applications, such as replacing cement concrete in various construc-

tion fields. Great efforts have been made in the concrete industry to use waste glass powder for the purpose of partially replacing cement when used as a filler, as it contains SiO_2 and therefore can replace cement to some extent in the concrete industry, as confirmed by researchers [11, 12].

Studies carried out by Choudhary, Kumar and Gupta [13] have shown that mixtures without fillers burn continuously until they are completely consumed, and as the metal filler content increases, the burning time decreases. The addition of mineral fillers allows these compounds to move from class M3 for moderately flammable materials to class M2 for highly flammable materials, according to the M classification for building and furnishing materials, such as the use of waste glass powder to form flexible pavements with satisfactory engineering performance and in an environmentally friendly and cost-effective manner as an alternative to limestone [14].

Atiqah et al. [15] confirmed that the use of glass powder in the polymer leads to an increase in mechanical properties such as tensile strength and an increase in Young's modulus. In addition, glass powders create visual and textural effects on the polymer surface, making it more aesthetically pleasing.

2. Experimental method

2.1. Materials used in the research

2.1.1. Network material: unsaturated polyester (UPE)

UPE from Akpa Kimya (Turkish origin) of density of 1.17 g/cm is a transparent, viscous liquid at room temperature and belongs to the group of thermosetting polymers (thermosets). It becomes solid when hardener is added, which contains two types of substances that help it to solidify: ethyl methyl ketone peroxide (as an initiator of the polymerisation process), which is a colourless liquid, and tin-2-ethyl hexanoate, which speeds up the decomposition of the initiator and is an oily liquid with a purple colour. The hardener is added to the UPE and mixed by adding 100 g of resin to 2 g of hardener. Once the addition of hardener and catalyst to the resin mixture is complete, the mixing process begins immediately by manual mixing for two to three minutes until the mixture is homogeneous. If this time is exceeded, the mixture becomes very viscous and its temperature rises, causing the melting process to accelerate. This hampers the casting process and the final product, which contains a lot of air bubbles. UPE resin has good mechanical, electrical and thermal insulation properties.

2.1.2. Reinforcing material

Automotive glass (A. glass) powder is a non-biodegradable material due to its inert nature [16], it is used in composite materials to reduce material costs, somewhat improve mechanical properties such as toughness, compressive strength, high sound and electrical insulation, high chemical resistance and in some cases improve the thermal properties of the material. Glass is one of the most widely used materials, with annual global production estimated at over 130 million tonnes [15]. Glass powder with a particle size of 75 microns (200 mesh) is added using special sieves. Glass is a desirable material for many industrial applications as it offers unique properties such as transparency, chemical resistance and high



Fig. 1. Compressive strength test: a) mold used to prepare the samples, b) shape of the samples, c) device used to measure compressive strength
Rys. 1. Pomiar wytrzymałości na ściskanie: a) forma użyta do przygotowania próbek, b) kształt próbek, c) urządzenie pomiarowe

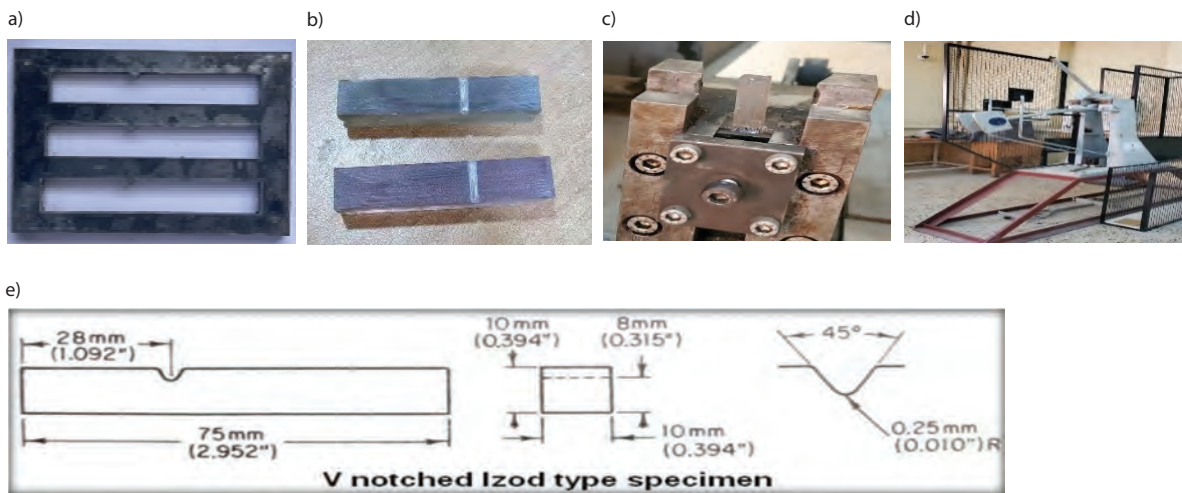


Fig. 2. Impact strength test: a) mold used to make samples, b) shape of the samples used for measurement, c) sample placed vertically in the Izod impact device, d) device used to measure impact strength, e) detailed chart of sample measurements and slitting used in Izod impact testing

Rys. 2. Pomiar udarności: a) forma do wykonania próbek, b) kształt próbek użytych do pomiaru, c) próbka umieszczona pionowo w urządzeniu do badań udarności, d) urządzenie do pomiaru udarności, e) szczegółowy schemat przebiegu pomiaru próbek i rozcinań

thermal resistance. The glass consisted of the following materials: sand (70%), soda (15%), limestone (10%) and other materials (5%) [17].

2.2. Preparation method

UPE was used after the addition of the hardener at a ratio of 2 : 100 to obtain a substance with a gelatinous consistency that hardens at room temperature (25°C). Materials based on automotive glass powder were prepared with different percentages by weight (5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, and 50%). Manual moulding technology was used, so that specific moulds were made for each dimension. The polyester was mixed with the purple hardener, then the glass powder was added and mixed well until homogeneity was achieved between the polyester and the powder. The transparent hardener was then added and mixed very slowly for a period of 30 s to 1 min to prevent air bubbles from forming in the overlapping materials, and then the moulds were left at room temperature for 24 h to allow the solidification process to take place and to complete the mixing and homogenisation of the molecules. The thermal effect of the prepared composites was studied to demonstrate the effect of winter and summer temperatures. For this purpose, the samples were placed at temperatures of 8°C and 50°C after removal from the mould.

2.3. Equipment used and sample preparation

2.3.1. Compressive strength test

The equipment used for the measurements was supplied by the Italian company Controls and the test samples were prepared according to American specifications (ASTM-D618). The samples were cylindrical in shape to withstand the maximum compressive load. A hydraulic piston type (50 t) was used to determine the maximum compressive load that the model could withstand (Fig. 1).

2.3.2. Impact strength test

The device employed was the Izod impact instrument, manufactured by Tokyo Koki Seizosho, Ltd. The test sample measured 10 × 10 × 75 mm, wherein a notch angle of 45° and a notch depth of 2 mm were created (Fig. 2). These specifications align with the American standard ASTM-D256-87.

2.3.3. Hardness strength test

The durometer Shore hardness testing device used was of the Shore D type and is manufactured by the German Wolpert company. The device resembles a compass, with a needle positioned centrally (Fig. 3). The testing procedure entails positioning the device at right angles to the sample until the needle is inserted into the material surface.



Fig. 3. The device Shore D used to measure hardness

Rys. 3. Urządzenie Shore D używane do pomiaru twardości



Fig. 4. Tensile strength test: a) mold used to prepare the samples, b) shape of the samples used for measurement, c) the device used to measure tensile strength

Rys. 4. Pomiar wytrzymałości na rozciąganie: a) forma użyta do przygotowania próbek do testów, b) kształt próbek użytych do pomiaru, c) urządzenie pomiarowe

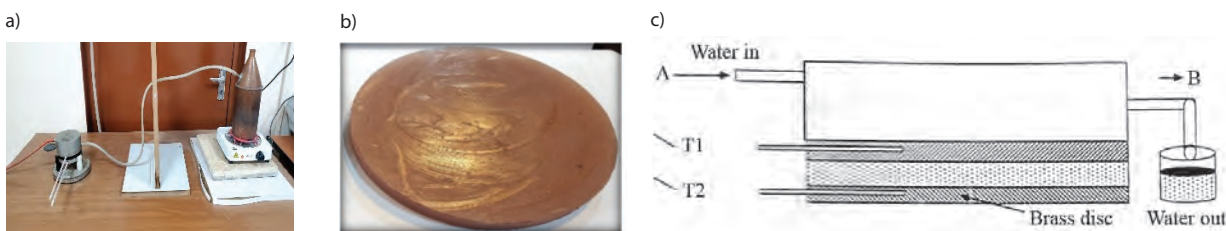


Fig. 5. Thermal conductivity test: a) device used to measure thermal conductivity, b) shape of the samples used for measurement, c) a diagram showing the mechanism of operation of the thermal conductivity device

Rys. 5. Pomiar przewodności cieplnej: a) urządzenie do pomiaru przewodności cieplnej, b) kształt próbek używanych w pomiarach, c) schemat działania urządzenia do pomiaru przewodności cieplnej

The subsequent reading of the hardness values is then conducted after a brief interval of approximately two to three seconds. To ensure the accuracy of the measurement values, it is essential that the measured models possess a flat surface, allowing for the device needle to be inserted vertically into the model.

2.3.4. Tensile strength test

The flexibility test is dependent upon the measurement of both elongation and stress. Consequently, the elongation test is performed on prepared samples with a thickness of 1 cm and a length of 20 cm (Fig. 4). The standard specifications (ISOR527) were adopted in the preparation of tensile strength test models (the models were in strips). This test was employed to ascertain the properties of the composite material under the influence of an axial load in two directions. The measurements were performed using the device (a universal test machine) produced by the American company Qualitest USA.

2.3.5. Thermal conductivity test

A disc device was employed for the purpose of measuring thermal conductivity (Fig. 5). The models were 11.23 cm in diameter and 1 cm thick [18] and were referred to as Lee discs. They were comprised of two halves. The upper half of the device consisted of a hollow metal cylinder with an opening through which steam can pass, while the lower half was also a cylindrical metal disc (made of lead or copper, whose specific heat capacity was known), and the two cylinders had the same diameter. Each disc featured a slot through which a thermometer may be inserted to measure the thermal conductivity coefficients, θ_1 and θ_2 . The prepared sample, whose thermal conductivity was to be measured, was placed between the two discs and was of the same diameter as the disk.

The temperature of the two thermometers was recorded every minute, and then the thermal conductivity equation was applied to find the thermal conductivity coefficient λ , as shown in the equation [19]:

$$\lambda \cdot \frac{1}{4}\pi^2 \left(D \frac{\theta_2 - \theta_1}{d} \right) = \text{mass of disc} \cdot C_s \cdot \text{Slop} \cdot \frac{1}{60t} \quad (1)$$

where:

D – diameter of the disc (sample) [cm],
 θ_1 – temperature of the thermostat in the upper dial [°C],
 θ_2 – temperature of the thermostat in the lower dial [°C],
 d – thickness of the disc (sample) [cm],
 C_s – specific heat capacity of the tablet [J/g °C],
 λ – thermal conductivity coefficient [W/(m · K)],
 mass of disc – mass of the device's disc [g].

2.3.6. Thermogravimetric analysis device (TGA)

The device employed for thermogravimetric analysis was a Mettler Toledo ultra-micro balance, comprising an electric oven containing a highly sensitive platinum balance. A sample weighing between 6 mg and 12 mg is placed in the oven, which is then heated at a gradual pace of no more than 10°/min, as indicated on the monitor. A graph is produced which illustrates the quantity of weight loss in the sample occurring during the elevated sample temperature. The weight of the sample is monitored continuously until the degradation process is complete in the designated sample area, referred to as the "pan". This is a specialized container used in the TGA device for examining the sample. At the conclusion of the weight measurement, the recorded weights are converted to a ratio representing the remaining sample weight at each measured temperature



Fig. 6. The thermogravimetric analysis device

Rys. 6. Urządzenie do analizy termogravimetrycznej



Fig. 7. A scanning electron microscope

Rys. 7. Skaningowy mikroskop elektronyowy

a)

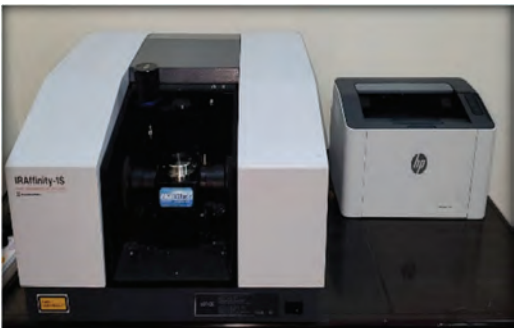
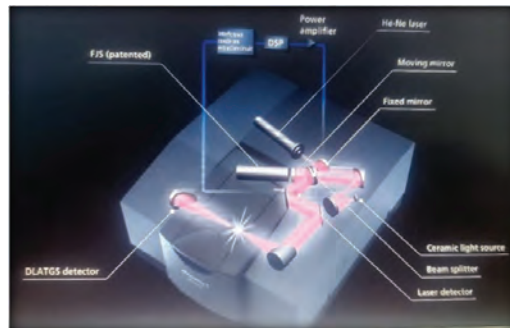


Fig. 8. Infrared spectrometer: a) device, b) mechanism of operation

Rys. 8. Spektrometr podczerwieni: a) urządzenie, b) mechanizm działania

b)



degree. The illustration depicts the thermogravimetric analyser (Fig. 6).

2.3.7. Scanning electron microscope (SEM)

A scanning electron microscope is a device that produces visual images by scanning a sample with a concentrated beam of electrons. The electrons interact with the atoms in the sample, producing a variety of signals that contain information about the surface topography and composition of the sample. The electron beam is typically surveyed using the dot scan, with the position of the beam combined with the signal to produce an image. The most common method of scanning is to detect secondary electrons from atoms raised by an electron beam. The image (Fig. 7) outlines the basic concept of the device's operation.

2.3.8. Infrared spectroscopy device (IR)

In both research and industry, IR is a commonly employed, straightforward, dependable, and efficacious method of measurement and quality control. It is especially employed in the field of forensic analysis in both civil and criminal cases. The advent of sophisticated computer technology and data processing has enabled the precise measurement of samples in solutions [20]. The degree of polymerization in the polymer industry can be quantified by measuring changes in the nature or quantity of bonds at a specific frequency over time. The device utilized in this study was the Japanese IRAffinity-1S type, manufactured by Shimadzu company. Examination is conducted by placing the sample in the form of powder

above the designated measuring lens, without the use of the KBR disc (Fig. 8). This technique is referred to as the IRA technique. It represents the latest measurement technique in infrared devices.

3. Results and discussion

3.1. Compressive strength test

The compressive strength test is a crucial method for evaluating the strength of a polymer and its resilience to the conditions under which it is used. There are many materials that may be brittle in the state of tension but appear ductile in the state of compression. Consequently, the examination of resistance to compressive strength is frequently employed in order to ascertain the yield strength, in addition to the compressive strength itself [21]. In general, the resistance to compressive strength is defined as the maximum stress that a solid can withstand without breaking or deforming under vertical pressure [22].

This test allows for the evaluation of the internal structural structure of the material being measured [23]. The material's resistance to compression before and after the consolidation process is calculated according to equation [24]:

$$\text{compressive strength [MPa]} = \text{force/area}, \quad (2)$$

where:

force – the applied force [N],

area – the sample's cross-section area, which is in the shape of a cylinder [m²].

Table 1. Compressive strength values of the UPE and UPE + A. glass at 25°C
Tabela 1. Wartości wytrzymałości na ściskanie UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) w temperaturze 25°C

Wt% at 25°C	Compressive strength: UPE [MPa]	Compressive strength: UPE + A. glass [MPa]
5	18.3	22.3
10	18.3	23.6
15	18.3	24.9
20	18.3	25.1
25	18.3	25.8
30	18.3	26.4
35	18.3	26.7
40	18.3	26.1
45	18.3	25.0
50	18.3	24.9

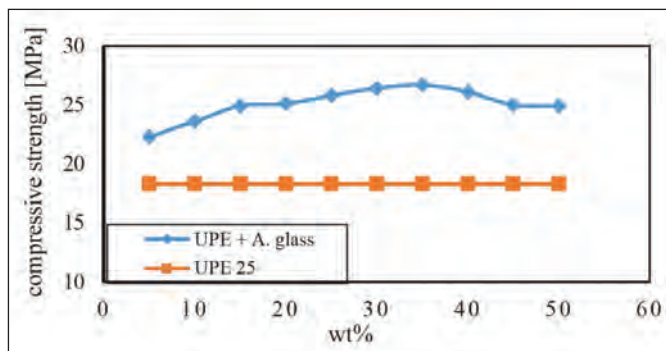


Fig. 9. The relationship between compressive strength and weight percentages of UPE and UPE + A. glass at 25°C

Rys. 9. Zależność między wytrzymałością na ściskanie a udziałem procentowym UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) w temperaturze 25°C

The results of the compressive strength values at 25°C, based on equation (1), showed that the material reinforced with A. glass powder has a higher compressive strength than the unreinforced material because the reinforcement material carries most of the stress applied to the material (Table 1, Fig. 9).

When the heat treatment was carried out at temperatures of 50.8°C, the compressive strength values of the samples at 50°C were found to be lower than those of the samples at 25°C and 8°C, because an increase in temperature causes an increase of the material's ductility as a result of the chains moving and the bonds holding them together to loosen, which in turn causes the compressive strength to decrease [25]. However, as the temperature decreases, i.e. at 8°C, the polymer chains become constrained and cannot move easily due to the lack of flexibility in the material, resulting in a high resistance to the force applied to the specimens, and thus the compressive strength increases [18] (Table 2, Fig. 10).

3.2. Impact strength test

Determining impact strength for polymers is very complex due to the multiple tests employed. The Garbi test and the Izod test are among the most important tests in this field. Impact strength testing is the measurement of a material's ability to resist fracture under the influence of an applied force, estimated in kJ and J [26]. Impact strength is very important from a practical point of view, as

Table 2. Compressive strength values of UPE and UPE + A. glass at 8°C, 25°C and 50°C

Tabela 2. Wartości wytrzymałości na ściskanie UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) w temperaturze 8°C, 25°C i 50°C

Temperature [°C]	Compressive strength: 30% UPE [MPa]	Compressive strength: 30% UPE + A. glass [MPa]
8	17.9	26.9
25	18.3	26.4
50	18.95	26.1

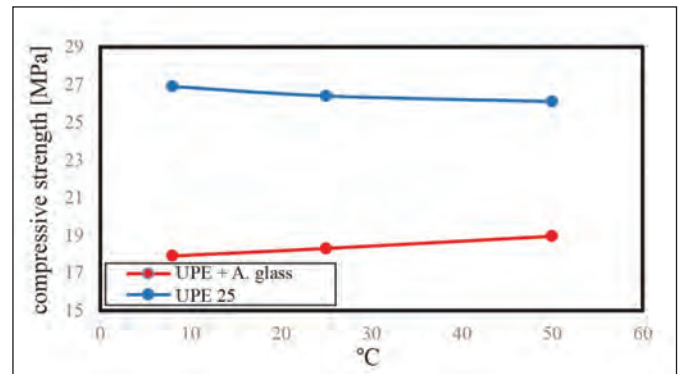


Fig. 10. Relationship between the compressive strength of UPE and UPE + A. glass and temperature 8°C, 25°C, and 50°C

Rys. 10. Zależność między wytrzymałością na ściskanie UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) a temperaturą 8°C, 25°C i 50°C

it allows us to determine the absorbed energy required to crush and break a sample, since this value is given directly by the testing device. The value is calculated using the following relationship [27, 28]:

$$\text{impact strength} = \frac{\text{fracture energy}}{\text{area}}, \quad (3)$$

where:

fracture energy – the energy absorbed by the model upon impact [kJ or J],

area – the cross-sectional area of the sample is a rectangle [m²].

Impact strength is generally considered low for UPE due to it being a brittle material, but after reinforcement with A. glass powder, we notice an increase in the impact strength values of the samples compared to what it was in unreinforced polyester. The reason for this is that the glass particles bear the bulk of the impact strength applied to the material. The A. glass powder improves this resistance, thus increasing the impact strength [29] (Table 3, Fig. 11).

When heat treatment is carried out at temperatures of 8°C and 50°C for samples with a UPE weight percentage of 30%, which is the best percentage chosen among the other percentages, the impact strength values decrease as the temperature decreases, i.e. at 8°C, to limit the ability of the chains to move. Therefore, it cannot move easily, but increasing the temperature will increase the movement, which is caused by the molecules of the polymeric compound breaking their bonds and increasing the movement of the polymeric chains at 50°C, which allows them to effectively

Table 3. Impact strength values of UPE and UPE + A. glass
Tabela 3. Wartości udarności UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass)

Wt% at 25°C	Impact strength: UPE [kJ/m ²]	Impact strength: UPE + A. glass [kJ/m ²]
5	18.5	18.9
10	18.5	19.1
15	18.5	19.3
20	18.5	19.7
25	18.5	19.8
30	18.5	20.1
35	18.5	20.0
40	18.5	19.8
45	18.5	19.1
50	18.5	18.6

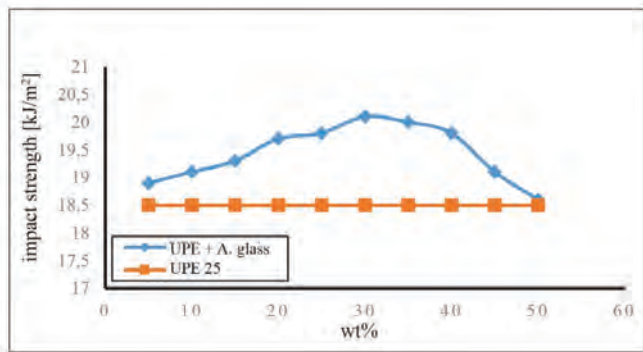


Fig. 11. Relationship between impact strength and weight percentages of UPE and UPE + A. glass at 25°C

Rys. 11. Zależność między udarnością a udziałem procentowym UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) w temperaturze 25°C

Table 4. Impact strength values of UPE and UPE + A. glass at 8°C, 25°C and 50°C

Tabela 4. Wartości udarności UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) w temperaturze 8°C, 25°C i 50°C

Temperature [°C]	Impact strength: 30% UPE [kJ/m ²]	Impact strength: 30% UPE + A. glass [kJ/m ²]
8	18.4	19.5
25	18.5	20.0
50	18.7	20.5

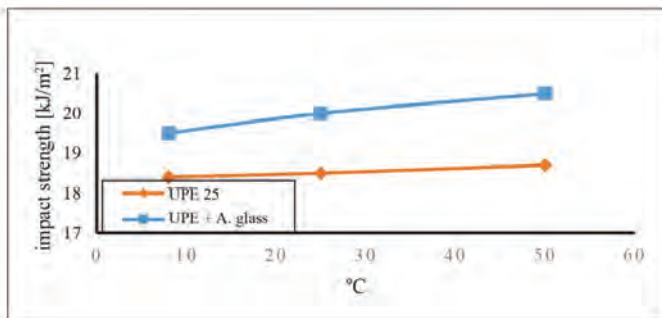


Fig. 12. Relationship between the impact strength of UPE and UPE + A. glass and temperature 8°C, 25°C and 50°C

Rys. 12. Zależność pomiędzy udarnością UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) a temperaturą 8°C, 25°C i 50°C

Table 5. Hardness strength values for UPE and UPE + A. glass at 25°C
Tabela 5. Wartości twardości UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) w temperaturze 25°C

Wt% at 25°C	Hardness strength: UPE	Hardness strength: UPE + A. glass
5	82.0	86.9
10	82.0	87.2
15	82.0	87.5
20	82.0	87.9
25	82.0	88.5
30	82.0	88.9
35	82.0	89.1
40	82.0	88.8
45	82.0	88.5
50	82.0	88.2

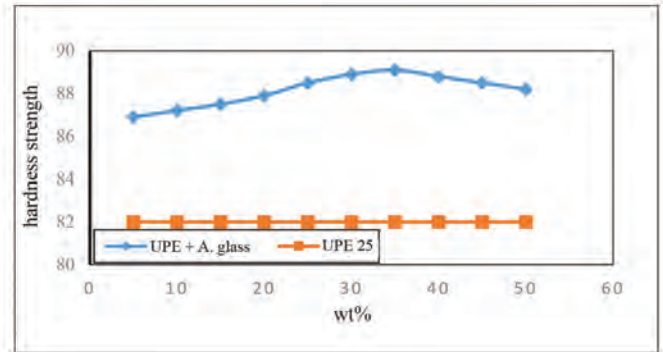


Fig. 13. The relationship between hardness strength and weight percentages of UPE and UPE + A. glass at 25°C

Rys. 13. Zależność między twardością a udziałem procentowym UPE i (UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) w temperaturze 25°C

absorb some of the energy and leads to the distribution and spread of the energy necessary for the fracture to occur in the form of mechanical dissolution [30] (Table 4, Fig. 12).

3.3. Hardness strength test

Materials may be subjected to scratching and penetration by harder equipment during their use in the field. Therefore, it is important to determine hardness, which can be defined as the resistance of the material surface to permanent deformation that can occur by cutting, abrasion, penetration and scratching [31]. Hardness tests are used to measure the resistance of a material to plastic deformation in its surface areas, using fine tips made of hard materials which can penetrate the hard material being tested [32]. The hardness of the material depends on the strength of the bond between atoms or molecules and the type of surface, as well as heat treatment and high temperature [33]. Reinforcing UPE + A. glass powder leads to an increase in hardness strength values due to increased cross-linking and interference between the UPE + A. glass powder and because the cross-linking reduces the movement of the polymer molecules and thus increases the hardness, which leads to increased resistance to deformation [34] (Table 5, Fig. 13).

Table 6. Hardness strength values of UPE and UPE + A. glass at 8°C, 25°C and 50°C**Tabela 6. Twardość UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) w temperaturze 8°C, 25°C i 50°C**

Temperature [°C]	Hardness strength: 30% UPE	Hardness strength: 30% UPE + A. glass
8	82.5	89.9
25	82.0	88.9
50	81.8	88.1

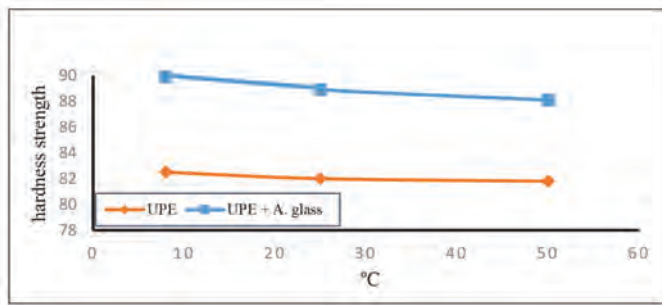


Fig. 14. The relationship between hardness strength for UPE and UPE + A. glass and temperature 8°C, 25°C and 50°C

Rys. 14. Zależność między twardością UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) a temperaturą 8°C, 25°C i 50°C

When carrying out heat treatment 8°, 50°C on samples with the content of 30%, chosen as the optimal percentage compared to the rest of the samples, we notice that the hardness resistance values were lower at 50°C than at 25°C as the increase in temperature leads to an increase in the ductility of the material due to the movement of the molecules and the breaking of the bonds between them, thus leading to a decrease in the resistance to scratches and punctures [35]. However, when the temperature drops to 8°C, we notice an increase in the hardness resistance values because the polymer chains are restricted and cannot move, therefore causing the material's resistance to scratches and punctures to increase (Table 6, Fig. 14).

3.4. Modulus of elasticity

Modulus of elasticity (Young's modulus) is a physical quantity that used to describe the material's resistance to deformation. It is defined as the ratio of stress to strain in a material when it is subjected to load [36]. When a material is stretched, compressed, or deformed, it will exhibit a certain amount of stress, which is the partial change in dimension. The modulus of elasticity determines how a material responds to this deformation. Understanding the modulus of elasticity is crucial to engineers and materials scientists, because it helps them design structures and materials that can withstand certain loads and stresses while maintaining their form and functionality. In addition, it is an essential parameter in the development of advanced materials, such as composites and metals, which are designed to have specific properties for particular applications. Resins are considered brittle materials, so the tensile strength of these materials is very low. When reinforcing materials are added, the tensile strength can be clearly improved. This is in order for the particles of the reinforcing material to wit stand the applied stress.

Table 7. Modulus of elasticity values UPE and UPE + A. glass at 25°C**Tabela 7. Moduł wartości elastyczności**

Wt% at 25°C	Modulus of elasticity: UPE [MPa]	Modulus of elasticity: UPE + A. glass [MPa]
5	3.2	2.944
10	3.2	3.098
15	3.2	2.955
20	3.2	2.913
25	3.2	2.903
30	3.2	2.885
35	3.2	2.831
40	3.2	2.801
45	3.2	2.709
50	3.2	2.644

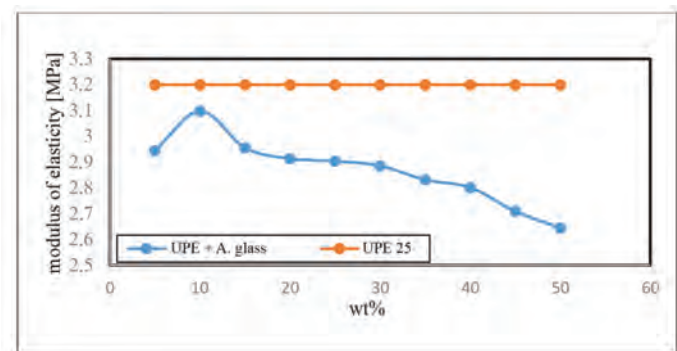


Fig. 15. Relationship between the modulus of elasticity and the weight percentages of UPE and UPE + A. glass at 25°C

Rys. 15. Zależność między modulem sprężystości a procentem wagowym UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) w temperaturze 25°C

Through research, the highest tensile strength by weight of 30% was obtained at a temperature of 25°C (Table 7, Fig. 15).

Choosing a weight percentage of 30% in heat treating at temperatures 8°C and 50°C we notice that the elasticity values decrease at a temperature of 50°C due to the disintegration of the polymer chains as a result of the high temperature. Conversely, as the temperature decreases, i.e. at 8°C, this leads to a decrease in the values. Flexibility is due to the binding of bonds and the movement of polymer chains, which makes them fragile [37, 38] (Table 8, Fig. 16).

3.5. Thermal conductivity

Thermal conductivity is defined as the ability of a material to transfer heat to two objects that have different temperatures, one of which has a higher temperature than the other. It is the ratio of the heat flow rate to the temperature difference. The relationship between thermal conductivity and temperature can be described by the Arrhenius equation (4) [39]:

$$k(T) = K^{\circ} \exp\left(-\frac{Ea}{kBT}\right), \quad (4)$$

where:

K° – the thermal conductivity at a reference temperature,

T – the absolute temperature,

Table 8. Modulus of elasticity values UPE and UPE + A. glass at 8°C, 25°C and 50°C

Tabela 8. Wartości modułu sprężystości UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) w 8°C, 25°C i 50°C

Temperature [°C]	Modulus of elasticity: 30% UPE [MPa]	Modulus of elasticity: 30% UPE + A. glass [MPa]
8	3.101	2.801
25	3.195	2.885
50	3.211	2.973

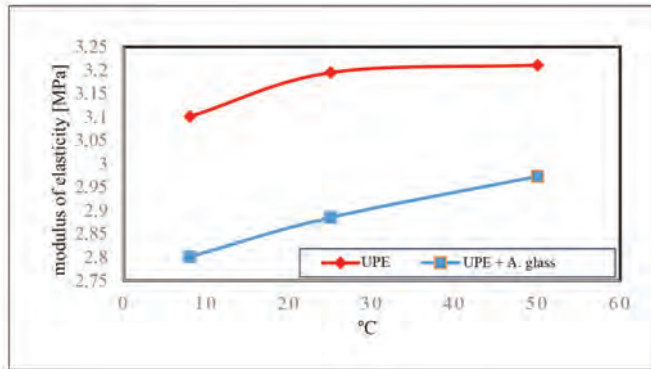


Fig. 16. Relationship between the modulus of elasticity of UPE and UPE + A. glass and temperature 8°C, 25°C and 50°C

Rys. 16. Zależność między modułem sprężystości UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) a temperaturą 8°C, 25°C i 50°C

K – the Boltzmann constant,
 Ea – the activation energy for thermal conductivity.

The variation of thermal conductivity with temperature can be understood in terms of the three main mechanisms that contribute to heat transfer:

- Phonon scattering – at low temperatures, thermal conductivity is determined primarily by phonon scattering, which is the scattering of phonons (quantum particles that represent the thermal vibrations of the material) by defects and impurities in the material. As the temperature increases, other scattering mechanisms become important in explaining the nature of phonon scattering.
- Electron transfer – at high temperatures, thermal energy can ionize atoms and molecules, producing free electrons and ions. These charge carriers can move through the material, contributing to thermal conductivity.
- Radiation – above a certain temperature, materials can emit electromagnetic radiation. Other materials can absorb this radiation, causing the temperature to rise and thermal conductivity to increase. However, this effect is usually limited to specific wavelengths and temperature ranges.

The thermal conductivity values show a decrease as the temperature decreases and an increase as the temperature increases, because at low temperatures the average kinetic energy of the molecules in the material is also lower. This means that there is less energy available to transfer heat through the material. Conversely, as the temperature increases, the average kinetic energy of the molecules increases, leading to more collisions and interactions

Table 9. Thermal conductivity values of UPE and UPE + A. glass at 8°C, 25°C and 50°C

Tabela 9. Wartości przewodności cieplnej UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) w temperaturze 8°C, 25°C i 50°C

Temperature [°C]	Thermal conductivity: 30% UPE [$W/m^2 \times 10^{-4}$]	Thermal conductivity: 30% UPE + A. glass [$W/m^2 \times 10^{-4}$]
8	2.556	2.469
25	2.616	2.508
50	2.739	2.592

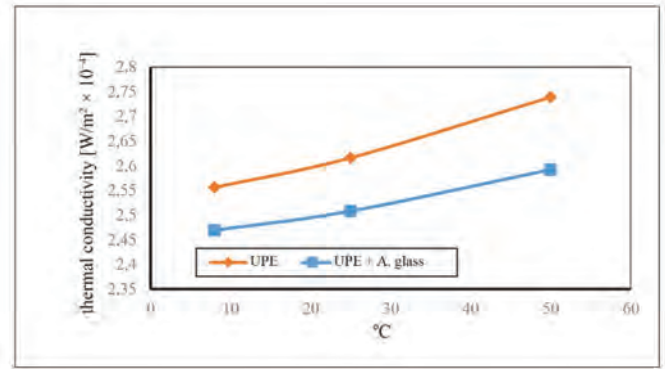


Fig. 17. Relationship between the thermal conductivity of UPE and UPE + A. glass and temperature 8°C, 25°C and 50°C

Rys. 17. Zależność między przewodnością cieplną UPE i UPE z dodatkiem szkła odpadowego przemysłu motoryzacyjnego (A. glass) a temperaturą 8°C, 25°C i 50°C

between molecules. This increased movement and collision of molecules allows for better heat transfer, resulting in increased thermal conductivity [40, 41]. In short, thermal conductivity is closely related to the average kinetic energy of the molecules in a material (Table 9, Fig. 17).

The thermal conductivity is lower thermal conductivity after the reinforcement process UPE and UPE + A. glass than before the reinforcement, because the polymers contain free electrons for heat transfer. The structural vibrations of the internal molecule, which depend on the thermal conductivity, are reduced when A. glass is added to unsaturated polyester, as glass generally has a lower thermal conductivity than polyester, because the glass molecules act as insulating barriers within the polyester matrix, reducing the movement of heat through the material where the glass molecules intersect to conduct heat, reducing the overall thermal conductivity of the composite. This makes the material more effective at insulating against heat transfer, resulting in lower thermal conductivity values.

3.6. Thermal stability of polymeric composite

The study of the concept of thermal stability is essential in material evaluation, as the stability of the material is a key factor in determining the suitability of the material for manufacturing and use. In recent times, the study of the analysis of the material has become increasingly important, and stability was measured through two axes: the first is the weighted heat analysis of changing heat (TGA), and the second is represented by the steady heat analysis (IGA), which measures the thermal stability of the samples by comparing

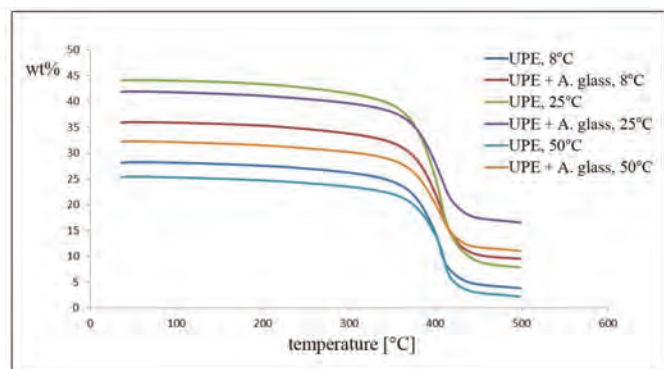


Fig. 18. TGA for UPE before and after reinforcement with A. glass at different temperatures: 8°C, 25°C, 50°C

Rys. 18. TGA UPE przed wzmocnieniem i po wzmocnieniu szkłem odpadowym przemysłu motoryzacyjnego (A. glass) w różnych temperaturach: 8°C, 25°C, 50°C

Table 10. IDT for treated polymeric composite at temperatures 8°C, 25°C and 50°C

Tabela 10. IDT poddanego obróbce kompozytu polimerowego w temperaturze 8°C, 25°C i 50°C

Polymeric composite	Temperature [°C]		
	8	25	50
UPE	350	360	375
UPE + A. glass	360	365	365

the temperature at the beginning and end of the decomposition. In addition, it determines the weight of the remaining article in the region that mediates the beginning and end of the decomposition. As a result, the following concepts were determined [42]: initial decomposition temperature (IDT) and complete decomposition temperature (CDT).

The values of both CDT and IDT were determined by identifying the point at which the change occurs and aligning it with the straight part of the curve at the beginning and end of the decomposition process. Fig. 18 illustrates the TGA decomposition curves of unsaturated polyester before and after reinforcement with A. glass at different temperatures (8°C, 25°C, and 50°C).

It is notable that the samples treated at 25°C have a lower degree of decomposition than those treated at 8°C or 50°C. This is due to the fact that an increase in temperature leads to the opening of polymer chains, which in turn increases the possibility of tangling the polymer chains more than at a temperature of 25°C. When treating samples at a temperature of 8°C, we observe a reduction in the temperature of the polymer decomposition from the treated samples at a temperature of 25°C. This is due to the tangling of the polymer chains with each other and the convergence of the remaining effective centres inside the chains, which are not allowed to interact with other centres. As the temperature rises to 50°C, we observe a transition from a completely overlapping state to a linear state for these chains. This allows the effective active centres to grow and complete the interaction, increasing their tangle with each other. Consequently, more heat is required for these samples than for the prepared samples at 25°C or 8°C.

From the drawing (Fig. 18), we can see that the change in value occurs at the intersection of the tangents and the straight

Table 11. CDT for treated polymeric composite at temperatures 8°C, 25°C and 50°C

Tabela 11. CDT poddanego obróbce kompozytu polimerowego w temperaturze 8°C, 25°C i 50°C

Polymeric composite	Temperature [°C]		
	8	25	50
UPE	440	440	440
UPE + A. glass	445	445	445

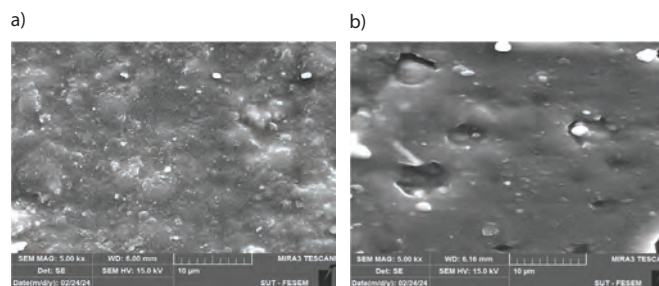


Fig. 19. Scanning electron microscope images: a) pure polyester, b) glass powder and polyester mixture

Rys. 19. Obrazy z elektronowego mikroskopu skaningowego: a) czysty poliester, b) mieszanka proszku szklanego i poliestru

part of the curve at the CDT. Prior to reinforcement, the CDT for UPE was 440°C. Following reinforcement with A. glass, the value was 445°C, indicating a slight increase. The CDT of UPE is attributed to the presence of the reinforcement material, which has the effect of raising the CDT of UPE. This is one of the characteristics of the reinforcement material, as it has the effect of raising the CDT of UPE, even if the temperature rise was slight. From the above, we can say that the introduction of a filler material, such as A. glass powder, has the effect of raising the CDT of UPE [43].

3.7. Scanning electron microscope (SEM)

The scanning electron microscope images of pure polyester and the mixture of glass powder and polyester are shown in Fig. 19. The average grain size increased from 17.28 nm for pure polyester to 81.81 nm for the mixture as a result of the aggregation of the polyester grains around A. glass powder particles. The samples' surface image also shows the extremely homogenous distribution of the glass powder. In addition, it also reveals the appearance of several cavities on the sample surface as a result of the mixing process.

3.8. Infrared spectroscopy (IR)

The IR of UPE before reinforcement demonstrated that different bands belonged to the most important functional groups present in the UPE, including the hydroxyl and carbonyl groups, the bond stretching C=C, the bond stretching CO=C, and the stretching vibrations OH.

The IR of UPE after reinforcement with A. glass did not show any significant change, which confirms that the behaviour of this material is limited to that of fillers (Fig. 20, 21). This is because the material is inert and chemically stable, and therefore adding it to UPE may have a limited effect on the wave numbers of the beams.

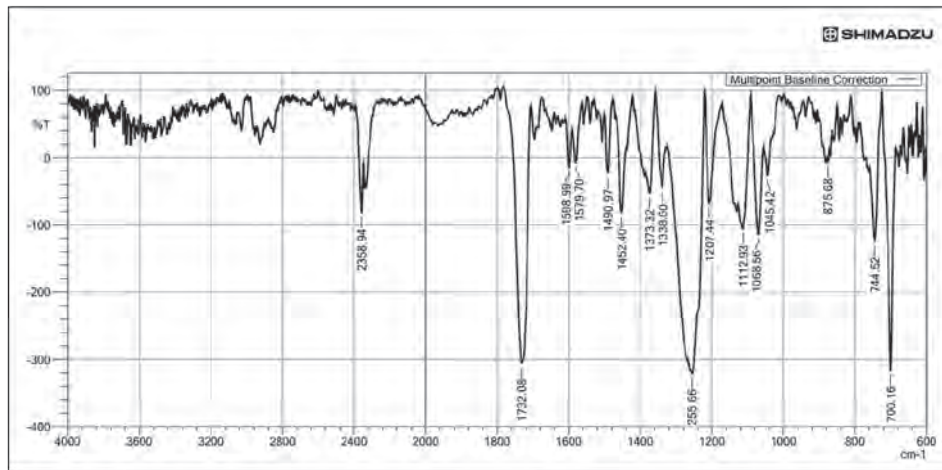


Fig. 20. IR of UPE before reinforcement

Rys. 20. IR dla UPE przed wzmocnieniem

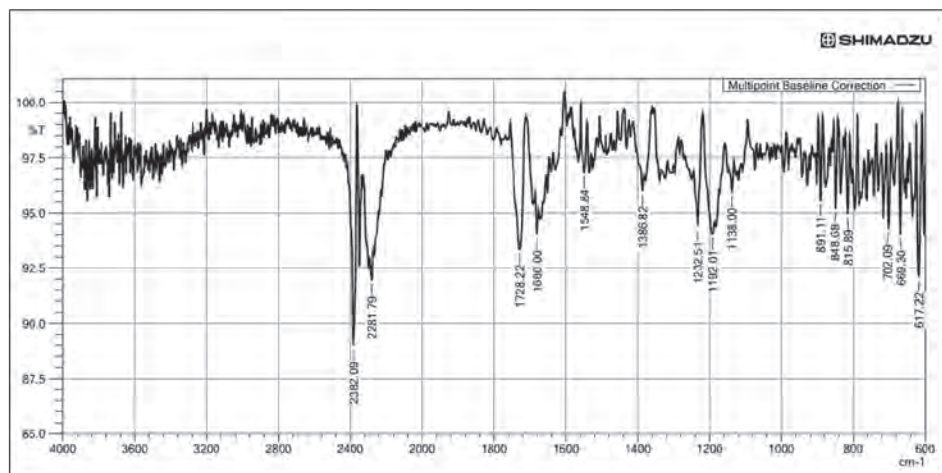


Fig. 21. IR for UPE after reinforcement with A. glass powder

Rys. 21. IR dla UPE po wzmocnieniu proszkiem szklanym

4. Conclusions

- Adding A. glass powder to UPE led to an increase in mechanical property values, i.e. an increase in compressive strength from 18.3 MPa to 26.4 MPa, impact strength from 18.5 kJ/m² to 20.0 kJ/m² and hardness from 82.0 to 88.9, while the modulus of elasticity decreased from 3.2 MPa to 2.885 MPa.
- When performing heat treatment on models after reinforcement with A. glass, we notice the following: when the temperature rises, the compressive strength values decrease from 26.9 MPa at 8°C to 26.1 MPa at 50°C, the impact strength values increase from 19.5 kJ/m² at 8°C to 20.5 kJ/m² at 50°C and the hardness strength values decrease from 89.9 at 8°C to 88.1 at 50°C, while the modulus of elasticity values increase from 2.801 MPa at 8°C to 2.973 MPa at 50°C.
- There was a decrease in thermal conductivity values from 2.616×10^{-4} W/m² to 2.508×10^{-4} W/m² after reinforcement due to the presence of glass, which is originally an insulating material.
- It was found that the CDT of UPE before reinforcement was 440°C, and after reinforcement it became 445°C, the reason for this change being the presence of the A. glass powder which raise the CDT.
- In the IR samples before and after reinforcement it was found that the bands that had appeared in the scheme remained

unchanged in both cases, however, these peaks decreased after adding A. glass, indicating that the support material did not interfere with the chemical composition of the UPE and it worked only as a filler materials.

- The SEM images showed that the measured patterns of the UPE were soft, which means that the UPE surface is not porous due to lack of voids or pores, but instead is crystalline. After reinforcement with A. glass powder, the images did not show any noticeable difference from the UPE images, except for some solids or lumps on the surface of the system, due to the solid materials added to the UPE. These results also confirm that the materials added to the UPE have no chemical effect on the UPE.

CRediT authorship contribution statement

Assis Ekhlash K. Hemadi: Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Kossay K. Al-Ahmady: Conceptualization, Data curation, Software.

Ebtahag Z. Sulyman: Conceptualization, Data curation, Formal analysis, Software.

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