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Electrical Resistance, Stability and Mechanical Properties of PVC Composites Containing Graphite and Semiconductor for Sensor Technologies

Bircan DİNDAR *[1], Anıl EKER[2]

Abstract

This study aimed to obtain a new flexible poly vinyl chloride (PVC) based composite with conductive or semiconductor properties. Additives were graphite and semiconductor zinc oxide (ZnO). A non-ionic surfactant was also firstly used to obtain a homogeneous composite. For the characterization of these new composites; humidification, electrostatic discharge (ESD), electrical resistance, thermal shock measurements, tensile test and morphological and microscopic (SEM) measurements were performed. For the light test, a “Solar simulator” with a 1000 W xenon lamp was used. The electrical resistance and tensile strength of the materials were measured at each test step. According to the data obtained, it was determined that the electrical resistance of the materials with high graphite content, without ZnO, is still stable, while the electrical resistance of the ZnO-doped materials decreases and their conductivity increases considerably in special stimuli such as light. P3G2Z (32% PVC, 60% Graphite, 8% ZnO) was greater than 3 MΩ, with a large change in conductivity after electrostatic discharge, reaching 1078.33 kΩ, with the largest difference observed. It was determined that the resistance of P2G3Z and P1G1Z composite materials under solar radiation decreased approximately 81 and 23 times, respectively. This event proves that the composites become light sensitive semiconductor. As a result, the electrical and mechanical data of flexible, sensitive, conductive and semiconductor new polymers by doping PVC with graphite and ZnO nanoparticles at different rates will make a great contribution to the sensor, actuator, management system control mechanisms, and the robots used in the automotive and defense industries.

Keywords: PVC composite, graphite, zinc oxide, conductivity, tensile strength

1. INTRODUCTION

Poly vinyl chlorid (PVC) is one of the most used plastic materials to ease our daily life. Used in many fields such as electrical cables, building materials, plastic bottles and flexible film production, PVC occupies an important place in the plastic market. Although, it is not very up-to- date, Ron Babinsky's article in 2007 states that there was over 30 billion kg

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of PVC production in 2004 [1]. Therefore, its characteristics have an important subject in industry to produce better PVC products. Glass transition temperature of PVC was determined as 87 °C and melting temperature as 212 °C. The degradation process starts from 250 °C [1, 2]. In this respect, PVC is easier to recycle than other common plastics. In our study on PVC with graphite and ZnO additives, it is aimed to be used for various purposes (like sensor etc.). In other words, by preparing some composites of PVC, new products that can be used in different sectors can be proposed.

Another consideration point is the stability of PVC without degradation. As it is shown in many previous studies, PVC degradation is triggered and accelerated by UV and high temperature [3-9].

In these studies, PVC was dopped with various materials like CNT, $FeCl_3$, $CoCl_2$ [3], hydrotalcite [4], cardanol acetate etc. to improve thermal stability which means decelerated degradation over time. The main purpose of the degradation when exposed to UV or heat is HCl emission of PVC which causes more degradation and polyene structures inside PVC [5,6]. In some cases, additive may also be toxic to environment which also causes damage to nature during degradation [7-8 9].

Carbon is one of the building blocks of organic materials. It is an element that has been known and used for a long time by humanity. Although coal and diamond forms are the most known, other forms of carbon also have unique properties. Carbon forms, which tend to change the mechanical strength and conductivity of the material to which it is added, opened the way for alternative composite materials that are lighter and cheaper than metals but with similar functions.

The strength and conductivity level of the composite materials (like PVC + graphite) to be produced by controlling the carbon addition rate can be adjusted according to the specific values desired [10-12]. Thanks to these controllable features, very small sizes of electronic circuit elements (transistors, resistors, diodes etc.) could be produced so electronic and computer technologies have been improved. It is possible to produce solutions for sound isolation [13], increased level of flame retardancy and decomposition retardancy [14,15]. Tripathi et al. stated that by adding graphite to a polymer, a new path or chain can be formed in the characteristics of the insulating polymer matrix [16].

In the future, in the manufacture of high storage and safe batteries, graphene and similar carbon structures that are targeted to use can contribute very much. It is important that efficient use and the storage of renewable energy in a period where it is aimed to diminish carbon dioxide emissions.

Within the scope of this study, it is primarily aimed to prepare PVC polymer composites that can serve the automotive and sensor industries. In this context, natural graphite and semiconductor ZnO were preferred as additive materials. Initially, new materials with high graphite ratios between 32-60% and doped with ZnO in some samples were prepared. It is aimed to measure the changes in electrical resistance and mechanical properties by applying environmental standard tests in all PVC polymer composite variations prepared.

During the production of the materials, the polymer material dissolved in the organic solvent medium was formed into a film in petri dishes by doping with graphene in micro sizes and ZnO in nano sizes in the ultrasonic hot-bath system. The layers were obtained by drying them homogeneously under low vacuum at room temperature in a vacuum oven. This work is original with its method and additives. The electrical resistances of all the composite layers obtained were measured after they were subjected to physical and mechanical standard tests. [6-9]

With the inclusion of semiconductor zinc oxide in the composite, it has been observed that the material changes from insulator to conductor with time and environmental effects. [12,16] According to the data obtained, it is possible that various variations of these composites will find application in different electronics or sensor sectors. However, in order to say that some materials are stable in terms of maintaining their electrical resistance, it may be necessary to check their repeatability over a very long period of time, and it can also open up new application areas.

2. MATERIAL AND METHODS

2.1. Materials

Within the scope of this study, S23/59 coded polyvinyl chloride (PVC), a fine-grained polymer material of Petkim Petrokimya Holding A.Ş. THF solvent of 99.9% purity and zinc oxide (ZnO) were obtained from Sigma-Aldrich (commercial product). Materials used in the working environment such as ethanol, chloroform, acetone, surfactant, Triton X-100 ($C_8H_{17}C_6H_4(OCH_2CH_2)nOH$) were purchased from Merck. Natural graphite was obtained from Kütahya Karabacak Mine Works. Structural properties of graphite like this 90% of them have grain size less than 300 mesh, density (d): 2.09 g/cm^3, surface area: 15.56 m^2/g. The chemicals were used as received without further purification. The distilled water was used during the studies was obtained from the ultrapure water system (Millipore-Q).

2.2. Methods

2.2.1. Preparation of PVC composite samples

First of all, tetrahydrofuran (THF) organic solvent is added to the fine-grained polyvinyl chloride (PVC) polymer material and mixed in an ultrasonic vibrating bath at 50-55°C. A homogeneous solution is obtained by completing the dissolution in a mixing time of 45 minutes. Then, graphite and/or ZnO are added and mixing continues for a while in order to obtain composites with different properties with doping at different percentages. In the next step, the mixture was spread in a thin layer in the glass petri dish and kept in a vacuum oven at room temperature at 0.5 bar pressure for 120 minutes to dry moderately. Figure 1 shows the flowchart of this procedure.

In the first experiments of the drying process, when working at 80°C and 55°C and 1 atm pressure (room condition), two important problems were encountered; First, due to the density of the graphite, it precipitated more in the lower part of the layer, so a homogeneous film layer could not be obtained. Secondly, it was observed that there was a visible roughness on the surface as a result of drying at room conditions. It was observed that the deformation occurred more on the rough surface due to the formation of bubbles during rapid evaporation. It was seen that the drying temperature is an important factor in the homogeneous formation of the composite product.

Various versions were studied until a homogeneous layer that would meet the optimum expectation was obtained. When the drying temperature was reduced to 25-30ºC, the deterioration of the surface was noticeably reduced. Since the decrease in temperature prolongs the drying time, it was found appropriate to reduce the ambient pressure to 0.5 bar by vacuuming. Under these conditions, the drying time took a minimum of two hours.

In this context, the study was focused on solving the problem-forming parameters. In order to slow down the naturally occurring precipitation due to the density difference and to obtain a film layer with a smooth surface, it was deemed appropriate to add Triton X-100 as a surfactant to the mixture during the composite preparation.

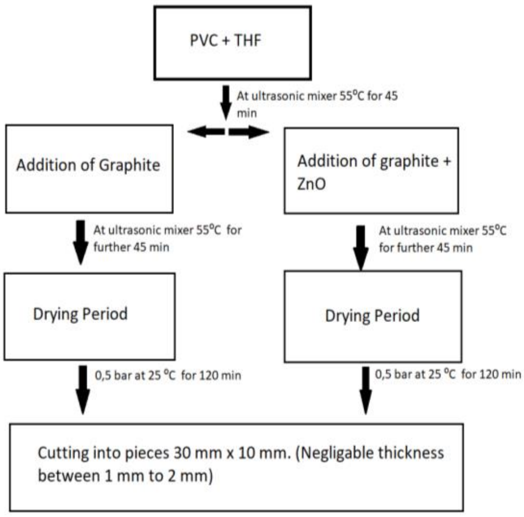

Figure 1 The production process of composite materials

Tritone X-100 provided a more homogeneous structure during and after the drying of the composite material. The graphite particles also remained at the same density above and below the film layer, so a very homogeneous layer was obtained.

Table 1 Components and code names of composite PVC samples

Material Code	Mixture Ratios	Mixture Amounts
P3G2	60% PVC, 40% Graphite	0.75 g PVC + 0.50 g Graphite
P3G2Z	60% PVC, 32% Graphite, 8% ZnO	0.75 g PVC + 0.40 g Graphite +0.10 g ZnO
P1G1	50% PVC, 50% Graphite	0.62 g PVC + 0.62 g Graphite
P1G1Z	50% PVC, 42% Graphite, 8% ZnO	0.62 g PVC + 0.52 g Graphite +0.10 g ZnO
P2G3	40% PVC, 60% Graphite	0.50 g PVC + 0.75 g Graphite
P2G3Z	32% PVC, 60% Graphite, 8% ZnO	0.50 g PVC + 0.65 g Graphite +0.10 g ZnO
P5	100% PVC	PVC 1.25 g

All composite types created within the scope of this study are listed below. The following abbreviation codes are used in the text to identify the materials produced in Table 1.

While the amounts of PVC and graphite varied in the variations created, the amounts of ZnO and Tritone X-100 (in the determined ratios, ZnO: 0.1 g and Tritone X-100: 0.148 mL) were kept constant. The deformation of the surface as a result of drying under normal atmospheric conditions with its temperature application is shown in Figure 2a. On the other hand, the composite layer obtained after the use of Tritone X-100 and slow evaporation in a vacuum oven is shown in Figure 2b.

In addition, heating, humidification, electrostatic discharge, exposure to sunlight and thermal shock were applied to each sample, respectively, within the scope of ambient climatization tests. After all these tests, electrical resistance measurements were repeated several times and data were collected.

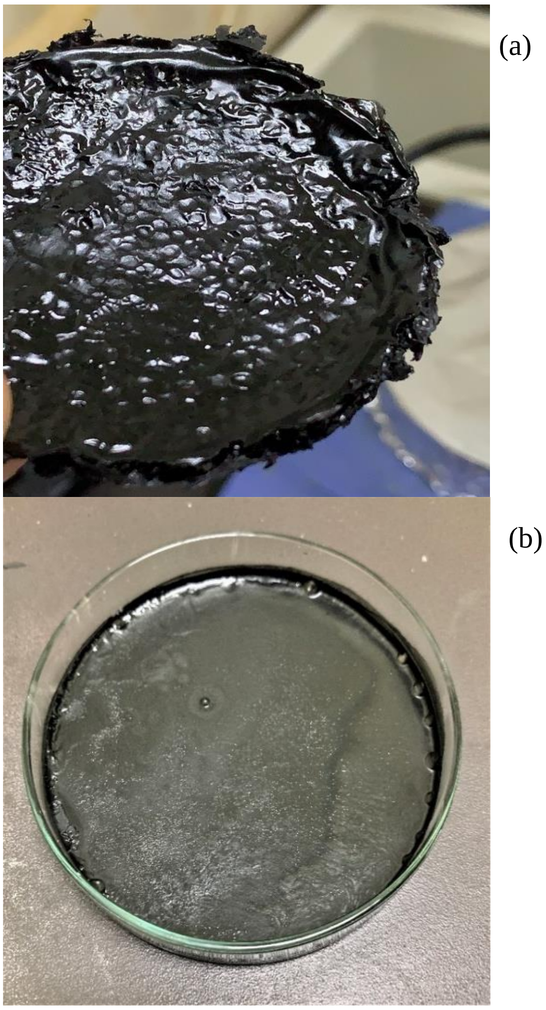

Figure 2 (a) Deformation over surface due to bubbles of fast evaporation, (b) Evaporation in vacuum and ambient temperatures with Triton X-100

2.2.2. Electrical resistance measurements

Hioki RM3548 device was used for electrical resistance measurements. In order to measure the electrical resistance of the newly produced composite materials, six strips of 30 mm x 10 mm were cut from each material, except P5. Three strips were prepared from P5 sample.

When measuring the resistance, the probes were placed 5 mm left and right from the middle of the sample. Therefore, the distance between the probes was fixed at 10 mm. The resistance was compared by averaging the resistance of six strips of each composite material.

2.2.3. Temperature test – heating

The glass transition temperature (Tg) of PVC, which has thermoplastic properties, is around 80°C, and it is a recyclable plastic. Generally, the usage temperature is between -50°C and +90°C. [9]

In this study, samples were kept on a hot plate at 100°C for one hour. This process causes the expansion of graphite as seen in some studies. Gorshenev and his colleagues found that graphite expands during the thermal process. [17] In addition, the glass transition temperature for PVC is exceeded. For this reason, the samples underwent some physical deterioration after this process, but no visible breakage and cracking occurred. Only plastic deformation was observed. Figure 3a, b shows the partial deformation after the heating test.

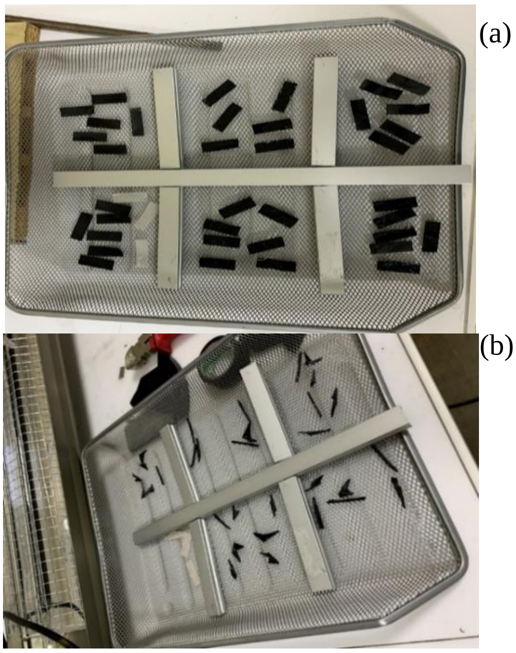

Figure 3 (a) Rectangular samples before heating, (b) Curling samples after heating

2.2.4. Humidification test

The samples were kept in the Nuve-TK252 humidification device at 40 °C for 96 hours at 85% relative humidity. Materials that absorb moisture may experience a decrease in resistance. The effect of this moistening process on the samples was recorded by electrical resistance measurement. This conditioning is based on damping conditioning in the automotive standard ISO 16750-4 Clause 5.7. [18] The humidification time interval is specified as 21 days in the standard.

However, in order to shorten the test interval and to see the effects instantly, it was decided to set the humidification time as 96 hours. Because measurements in previous studies have shown that the moisture absorption capacity of polymer materials in four days is close to the maximum level.

Studies were conducted with 96 hours of humidification as there was no appreciable difference in subsequent exposure time. 96 hours of humidification time is also among the technically used options. It was used in this study as well. The humidification time may vary according to the chemical structure, nature and expected moisture absorption of different materials.

2.2.5. Electrostatic discharge (ESD)

For testing the samples, Schloeder SESD30000 Electrostatic Discharge (ESD) device was used. This test involves transferring a static electricity charge of ± 15 kV to the samples via air discharge. 20 times static discharge, 10 times positive and 10 times negative, was applied to each sample. This test was carried out according to the conditions of the ISO 10605 standard [19] (Figure 4), 330 pF capacitor and 330ohm resistor were selected. The graph below shows the present-time curve of the ESD signal. Y: Current (A), X: Time (ns). In the standard, the graph is given for 5 kV (Figure 5).

Figure 4 ESD application to samples over copper coupling plate

330pF capacitor and 330ohm resistor were selected. The graph below shows the present-time curve of the ESD signal. Y: Current (A), X: Time (ns). In the standard, the graph is given for 5 kV (Figure 5).

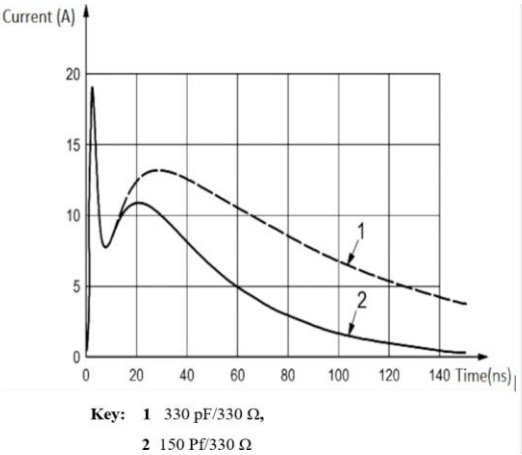

Figure 5 Current vs Time graph of electrostatic discharge of 5 kV potential applied with specific capacitance and resistance values to simulate natural ESD signals

2.2.6. Solar radiation test

For the light sensitivity test, a “Solar Simulator” with a 1000 W xenon lamp, which can be a precedent for natural sunlight, was used in the Photochemistry Laboratory of the Solar Energy Institute. Generally, most lamps have a narrow spectrum, while xenon lamp emits light with a broad spectrum in the ultraviolet-visible and near-infrared regions that are very simulated to sunlight. In some studies, the effect of light on the polymer was studied only under a UV light source. [20] However, a system that does not include visible region radiation is not an adequate example of sunlight emission.

For this test, called solar radiation, a high-power xenon lamp is used, which is placed in a rectangular cabinet with a mirror reflective, glossy interior surface to create a test setup similar to the spectrum and light intensity specified in the IEC 60068-2-5 standard. The maximum emission of the lamp is also in the wavelength range of 500-600 nm where the sun is at its maximum. In the laboratory environment, the samples were kept in an ice water bath in a 100 mL transparent container to protect them from the heat emission of the lamp and to observe the light effect only.

The samples were exposed to a light intensity of 1000 W/m^2 at a distance of about 10 cm from the lamp. In this way, the effect of high temperature is eliminated and only the effects of light on the samples are tried to be determined. [21] Test time with xenon lamp is limited to 2 hours (See Figure 6).

Figure 6 Solar radiation study with xenon lamp in the solar simulator in the laboratory

2.2.7. Thermal shock

Nuve FN120 and FR590 Thermal Shock devices were used to characterize the composites after the thermal shock test. In this test, samples are subjected to rapid temperature changes between -40 °C and +80 °C. Wetting time is 10 minutes in cold and hot regions, and the maximum determined transition time between regions is 30 seconds. One cold and one hot application means a total cycle of 20.5 minutes. In total this cycle is done five times. The operating conditions of this test are as defined in the 5.3.2 Rapid temperature change section of the ISO 16750-4 standard [22].

2.2.8. Tensile strength

Shimadzu EHF-LV020K2-020 device was used for the tensile test. Tensile strength measurements were made by comparison method.

In this study, samples that were not exposed to any environmental effects and stored in closed boxes at room conditions were identified with the prefix U-, and samples exposed to all environmental effects were identified with the prefix T-. For example;

PVC (U-P5): Only PVC sample that has not been exposed to any environmental effects and stored in a closed box under room conditions.

PVC (T-P5) : It is only for the PVC sample exposed to all environmental effects.

Icons of other samples;

U-P3G2Z, T-P3G2Z, U-P3G2, T-P3G2. P2G3, the best material for stable conductivity, was not tested for tensile testing.

2.2.9. SEM analysis

Scanning electron microscopy (SEM) is a characterization method. The Scientific Apreo S scanning electron microscope -SEM device was used to obtain SEM images of PVC-based composite samples and for the data of elemental analysis of Energy Distribution Spectroscopy (EDS). In this study, the surface morphologies of the PVC layers with graphite and/or ZnO doping at certain percentages, as well as the chemical components in their content were revealed.

3. RESULTS AND DISCUSSION

In this study, various organic solvents have been firstly tested in order to create the most cost-effective, easy procedure, and homogeneous dissolution of PVC under mild conditions while preparing composites by doping processes. After the solution conditions were determined, graphite and/or zinc oxide (ZnO) were added to the dissolved PVC solution, and new composites with different components and different properties were obtained. Graphite nano powder, insoluble in water or organic solvents, was suspended in solution in an ultrasonic homogenizer medium.

This process also contributes to the separation of graphite into thinner layers up to graphene. In this context, the added material can be separated into thin layers and penetrate further into the polymer matrix.

In this procedure, Triton-X 100 surfactant was chosen first time to achieve a homogeneous suspension and delay the precipitation of graphite particles after ultrasonic mixing was stopped. This contribution also makes the related work original.

By filling the parts in the polymer matrix that graphite cannot reach with ZnO atoms (nano particles, NPs) with semiconductor properties, the conductivity was changed and it was observed that the flexible composite also served the semiconductor property under the light test. In this study, the fact that a material with such semiconductor properties was obtained once again brings originality with a new product.

In some previous studies, there are some data on the electrical conductivity and mechanical strength of the thermoplastic-graphite composite, the differentiation of properties under [23] thermal and UV light. [24]

In this work, the electrical conductivity and mechanical strength of PVC-graphite and PVC-graphite-semiconductor ZnO composites firstly prepared at different percentages were compared with the pure PVC polymer material prepared under the same conditions. After this comparison, a material aging test program was created and as a result of this program, the changes in the conductivity and strength values of the aged samples were examined and revealed.

In the creation of the aging program, IEC (International Electrotechnical Commission) standards, which define environmental tests, and ISO (International Standards Organization) standards, which define environmental tests and industrial standards used by automotive manufacturers, were taken into account. [18,19, 22]

The reason for choosing these standards is to evaluate the natural conditions that materials will be exposed to in fields such as automotive, defense industry, aerospace, and optoelectronics. In addition, other studies in the literature were evaluated as a guide to predict which changes in the environment may affect material properties when choosing environmental test standards.

In conclusion, it is known that the electrical resistance and mechanical properties of these materials will change depending on humidity [18], UV radiation [20], thermal variations [17, 22], and voltage application [22, 25,26]. Also, the addition ratio is an important factor. When addition ratio of graphite is below %10, the composite’s tensile strength features can be increased. [23, 24] However, in this study graphite ratio is much higher than %10, thus more brittle structures were expected.

As a result of environmental examines, significant changes occur in the electrical resistance of materials. As the graphite ratio increases, the electrical resistance decreases. Mixtures of graphite and zinc oxide behave differently under different environmental conditions. That is, the initial resistance of P3G2 (60% PVC, 40% Graphite) was 503.61 kΩ, while P1G1 (50% PVC, 50% Graphite) measured 433.40 kΩ and P2G3 (40% PVC, 60% Graphite) measured 25.51 kΩ. It is seen that the material is becoming increasingly conductive. However, increasing the graphite addition rate causes losses in mechanical properties and at the same time, it becomes brittle by decreasing its flexibility. After heat treatment at 100 ºC for one hour, the resistances of the same samples also differ; In the presence of increasing graphite ratios such as P3G2, P1G1 and P2G3, resistors were obtained as 1166.37, 179.78, and 19.40 kΩ, in the order mentioned. In these measurements, the resistance increased after the temperature treatment in the matrix where the polymer was high [17], but in the matrix where the graphite ratio was high, the resistance decreased further after the temperature effect, causing the conductivity to increase. Sometimes, excessive and irregular placement of graphite particles will also cause defects, resulting in a decrease in electrical conductivity. [20]

After the same materials were exposed to light radiation, the resistance of the P3G2 sample became very high (>3 MΩ), while the lowest resistance (20.00 kΩ) was obtained in the P1G1 (50% PVC, 50% Graphite) sample, such that the best conductivity was obtained. It can be said that with the rearrangement and crystallization of graphite nanoparticles in the polymer matrix exposed to temperature and light for a certain time, the electrical conductivity gradually increased with the increase in the graphite concentration. [22,23] Since electrical conductivity occurs by electron transfer, graphite particles must also be within the jump distance of an electron. [22]

In semiconductor ZnO doped polymer composites, after exposure to light and thermal shock application, it is seen that the electrical resistance of the material decreases with the increase of graphene ratio in the matrix, that is, their conductivity increases. The P2G3Z (32% PVC, 60% Graphite, 8% ZnO) composite showed the best conductivity among the samples after exposure to light. Although the sample with the highest polymer component, such as P3G2Z (60% PVC, 32% Graphite, 8% ZnO), had small amounts of graphene and ZnO, the electrical resistivity was 3 MΩ even after being initially treated at 100 ºC for one hour and tested for humidity. have been greater than among the samples, the composite material that showed the least electrical resistance after the humidity test was P3G2 (60% PVC, 40% Graphite). Considering these properties of the produced composites, the suitability of the materials for use in places open to external factors can be evaluated in which sectors they will be used.

Consequence of environmental tests, significant changes occur in the electrical resistance of the materials. As the ratio of graphite increases, electrical resistance decreases. Graphite and zinc oxide mixtures behave differently under different environmental conditions. The increase in the graphite addition rate causes losses in mechanical properties. Considering these features of the produced materials, their suitability for use in places open to external factors can be evaluated.

3.1. Electrical Resistance

Instant measurements of electrical resistances after environmental condition applications (Table 2).

Consequently, it has been determined that the P3G2Z variation has high insulation (>3.00 M ohm). The most conductive one is P2G3. However, in this case, conductivity comes with brittleness. The most brittle material is also P2G3, and this is obviously seen with visual examination even before tensile strength.

Table 2 Instant average resistance values of samples for one hour at 100 ºC and humidity test

Material	Inıtial Resistance (kΩ)	After one Hour at 100 ºC (kΩ)	After Humidity test (kΩ)
P3G2	503.61	1166.37	63.25
P3G2Z	>3.00 MΩ	>3.00MΩ	>3.00 MΩ
P1G1	433.40	179.78	238.00
P1G1Z	585.55	680.00	301.00
P2G3	25.51	19.40	84.30
P2G3Z	981.10	285.50	218.00

After the tests, the highest difference in conductivity is also observed in P3G2Z, it even can be considered conductive after tests. The critical condition that changes conductivity of P3G2Z is ESD (From 3M ohm to 1M ohm). (Table 3) While solar radiation increased conductivity in this variation, thermal shock has not significantly affected conductivity.

All resistance measurements after solar condition were made in ambient room condition. The change in electrical resistance in the P3G2 sample showed different tendencies towards conductivity and insulating according to environmental conditions.

As the graphite ratio in other samples increased, more conductive samples were obtained from the first resistance. It has been determined that ESD and solar radiation increase conductivity in variations containing zinc oxide.

Table 3 Instant average resistance values of samples for solar radiation and thermal shock test

Material	After ESD (kΩ)	After Solar Radiation (kΩ)	After Thermal Shock (kΩ)
P3G2	952.00	>3.00 MΩ	372.00
P3G2Z	1078.33	912.00	968.00
P1G1	403.80	20.00	55.60
P1G1Z	106.50	24.30	109.30
P2G3	142.00	39.25	20.30
P2G3Z	106.00	12.40	73.30

Although the resistance change in mixtures without zinc oxide shows trends in different directions such as P3G2, more conductivity was observed than this. When the first resistance and final resistance measurements were compared, it was seen that the least difference was in P2G3. However, this material has more brittle construction due to high graphite ratio.

The variations of same ratio of PVC and graphite had been affected in each test.

In addition to the effect of solar radiation on electrical resistance, it has been determined that it causes whitening in P3G2 and P3G2Z samples
where PVC ratio is high. As the PVC rate decreases, it is seen that the sample retains its blackness better.

3.2. Tensile Strength

The tensile strength test was studied with the help of the Shimadzu EHF-LV020K2-020 device, using the comparison method.
In this study, samples that are not exposed to any environmental impact are indicated with the prefix U-, and samples that are exposed to environmental impacts are indicated with the prefix T-. For example, the polymer material indicated by U-P5 has not been exposed to any environmental influences. PVC, shown as T-P5, has also been exposed to all environmental effects.

The symbols of other samples are shown as U-P3G2Z, T-P3G2Z, U-P3G2, T-P3G2. The tensile test could not be performed as the P2G3 composite became quite rigid with 60% graphene content. However, this material was quite good in terms of conductivity. Initially 25.51kΩ, the most change of resistance was 142.00 kΩ after ESD application.

The electrical measurements taken in the other test results were very close to the initial value. It has been observed that this material has a high graphite content and a brittle structure. For this reason, materials close to pure PVC in terms of strength were selected for mechanical comparison. The stability in conductivity caused losses in terms of mechanical strength. A strip (30 mm x 10 mm) of the six different variations above was tested. The results are shown in Table 4.

Table 4 Tensile strength measurements of chosen samples

Material	Max. Stress (N/mm²)	Max. Elongation (%)	Elastic Modulus (N/mm²)	Energy (J)
U-P5	67.48	3.50	2702.20	0.09
T-P5	38.17	7.69	1654.03	0.09
U-P3G2	28.93	2.06	1949.11	-0.01
T-P3G2	18.76	5.93	1025.13	0.04
U-P3G2Z	20.05	2.74	1084.67	0.01
T-P3G2Z	31.85	3.27	---	0.01

Keeping the graphite mix ratios high seems to reduce the maximum tensile stress of the material. It was determined that zinc oxide additive provided improvement in tensile strength after all environmental tests. In other variations, environmental testing reduces strength, while in the zinc oxide variation the opposite is true. As we have seen in other studies in the literature, it is necessary to determine the optimum graphite additive ratio in order to strengthen the material. In this study, since conductivity was prioritized, graphite additive ratios as mass percentage were kept high, and therefore, a decrease in strength occurred. Pure PVC is a softer material and can carry more energy until it breaks.

3.3. SEM Analysis

Thermo Scientific Apreo S scanning electron microscope (SEM) device was used for obtaining SEM images and elemental analysis of Energy Dispersive Spectroscopy (EDS).

In this study, the films formed by dispersing certain percentages of graphite and/or ZnO in PVC solution by an ultrasonic process were examined using scanning electron microscopy (SEM). The surface morphology and elemental components of the P3G2 (60%

PVC, 40% Graphite) composite material are shown in Figure 7(a and b).

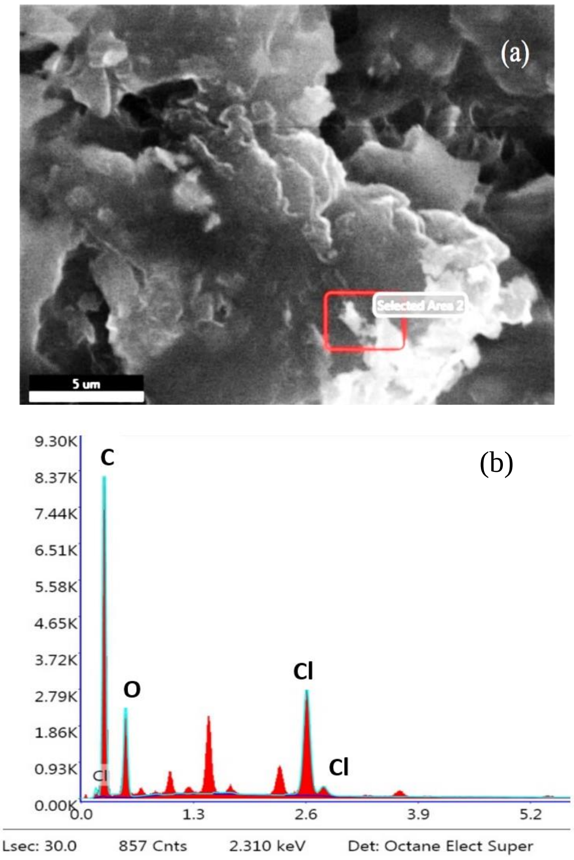

Figure 7 (a) SEM image of P3G2 material, (b) Elemental analysis of the region of P3G2 material

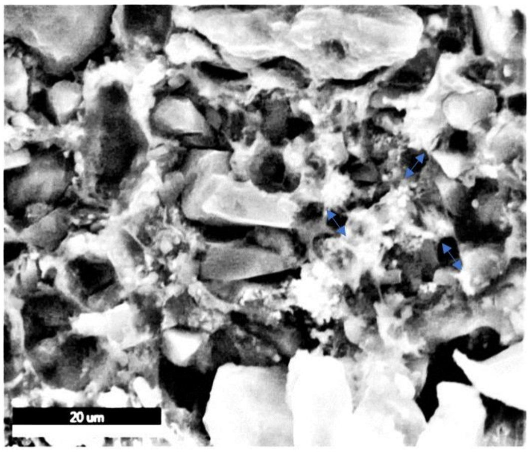

Figure 8 SEM image of P3G2Z material

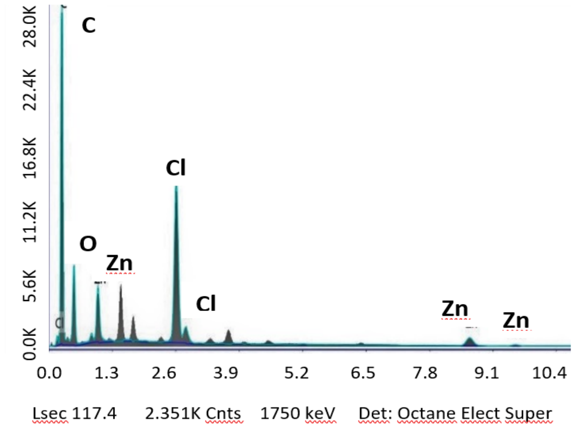

Figure 9 Elemental analysis graph of P3G2Z material in the EDS measurement (components: C, Cl, Zn, and O)

Since 60% of the main component of the material is PVC, the SEM images of the surface show that it is rather smooth and more homogeneous, which is compatible with the literature. [20, 26, 27] Here, it is seen that the carbon atoms are in large heaps due to the high polymer material ratio.

Figures 8 and 9 below show the morphological images and elemental analysis of the P3G2Z material in SEM and the graphite and semiconductor ZnO regions. However, micro-voids (large porous regions) are observed in the material under the influence of environmental tests. The fact that the crystal-like structures in the middle contain high concentrations of carbon without other elements indicates that these regions are graphite.

When the atoms in the image are mapped as a result of the EDS analysis, it is distinguished that PVC consisting of a combination of Cl-C (Chlorine-Carbon) atoms, [20] graphite consisting of only carbon atoms and ZnO consisting of zinc and oxygen atoms are separately distinguished.

As predicted at the beginning of the study, ZnO nanoparticles smaller than graphite with micron particles fill the gaps that graphite cannot fill. The production of composites with the help of the ultrasonic mixing system also played an important role in the homogenization of the materials.

In SEM morphology, the smaller crystals in between confirm the presence of green-colored zinc oxide (Figure 10). It is seen that the amount of zinc also less than red-colored graphite.

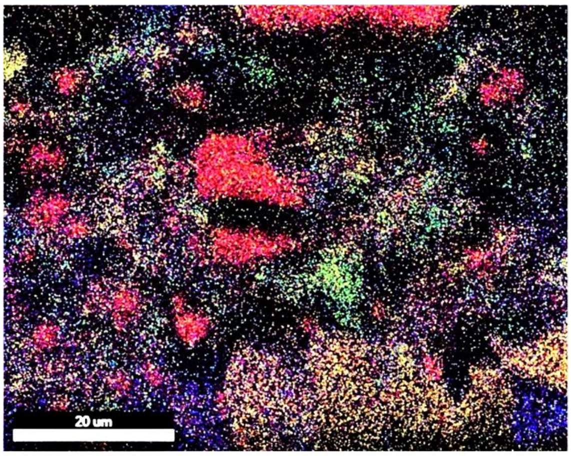

Figure 10 A colored image of EDS analysis of P3G2Z material. The red zone in the middle belongs to graphite. The green parts belong to ZnO

As seen in previous studies, graphite is clustered in the form of large cubes and rods, [14, 22] zinc oxide nanoparticles appear as smaller hexagonal bar crystals (wurtzite). [23]

4. CONCLUSION

Within the scope of this study, it was aimed to measure the electrical resistance in polymer composite variations with high graphite ratios between 32-60%. It has been found that the electrical resistance changes less and a more stable material is obtained when it is in high ratios. However, these materials have experienced some mechanical losses. Although the presence of semiconductor zinc oxide changes the material from insulator to conductor over time and with environmental effects, it can be suggested that some of its composites can be used as light sensors in applications. However, it may be necessary to check the repeatability over a very long period of time to say that the material is stable in terms of maintaining its electrical resistance.

When the peripheral tests are examined in detail, the following results are obtained: With holding in an air oven at 100°C, composites with increased graphite content, for example, P1G1 (50% PVC, 50% graphite), P2G3 (40% PVC, 60% graphite) and P2G3Z (32% PVC, 60% graphite), 8% ZnO) conductivity was also observed to increase.

As a result of the humidification tests, the proportionality of graphite such as P3G2 (60% PVC, 40% graphite), P1G1Z (50% PVC, 42% graphite, 8% ZnO) and P2G3Z (32% PVC, 60% graphite, 8% ZnO) It was found that the conductivity increased in the samples with increasing temperature. Moreover, the conductivity of composites containing all ZnO additives was increased after ESD and solar radiation. The P3G2Z material, which was subjected to ESD application, showed a great change and turned from an insulator to a conductor.

Solar radiation was also observed to increase conductivity at relatively high graphite ratios such as P1G1 (50% PVC, 50% graphite) and P2G3 (40% PVC, 60% graphite). It was found that the resistance of the P2G3Z composite, which contains the maximum graphite and ZnO additives from the products, decreased approximately 81 times, while the P1G1Z material decreased 23 times under solar radiation. This data proves that the related materials acquire photosensitive semiconductor properties.

P2G3 (40% PVC, 60% graphite) composite showed very good conductivity even when first prepared and became more conductive after thermal shock. It was observed that thermal shock only increased the conductivity of P2G3 (40% PVC, 60% graphite) and P3G2 (60% PVC, 40% graphite) materials.
Among the composites without any environmental treatment, the highest insulation belonged to P3G2Z and the highest conductivity belonged to P2G3.

In this study, conductivity measurements were instantaneously measured after environmental tests. Aging methods such as the "Arrhenius method" can also provide more information in terms of long-term stability. Thus, the obtained data are promising for the sensor and actuator sectors that move and/or control a mechanism and system. According to the needs of the application areas, it will be possible to produce materials or sensors in different capacities.

In conclusion, it can be suggested that the conductivity of composites in which the ZnO additive is a component increases considerably under solar radiation and that such composite materials have semiconductor properties, so they can be used in photosensitive control systems. The data obtained in this study are promising for the sensor and actuator sectors that move or control a mechanism and system.

In the future, in addition to sensor technologies, the use of graphene and semiconductor structures in the production of other new technologies such as high security and accumulators may contribute to both the literature and the development of new technological fields.

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Conflict of interest

We have read and understood journal policy on declaration of interests and declare that we have no competing interests. Ethics committee approval is not required declaration.

Authors' Contribution

Under this heading, the first author contributed 70%, the second author 30%.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that "Sakarya University Journal of Science" and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than "Sakarya University Journal of Science".

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