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## POLYMER COMPOSITES FOR 3D PRINTING

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Polymer composites for 3D printing, which are formed on the basis of photopolymer resin and inorganic filler, have been studied and obtained. Such polymer composites are obtained with more useful structural or functional properties. The inclusion of particles, fibers or nanomaterial reinforcements in polymers allows the manufacture of composites of polymer matrices, which are characterized by high mechanical properties and excellent functionality. Graphene with high electrical, thermal and mechanical properties is quite important as nanofiller in polymer matrices.

*Keywords:* 3D printing, polymer composites, graphene oxide, photopolymer resin, reinforcement.

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### 1. Introduction

3D printing is an additive manufacturing (AM) technique for fabricating a wide range of structures and complex geometries from three-dimensional (3D) model data. The process consists of printing successive layers of materials that are formed on top of each other. Charles Hull has developed this technology in 1986 in a process known as stereolithography (SLA), which was followed by subsequent developments such as powder bed fusion, fused deposition modelling (FDM), inkjet printing and contour crafting (CC). 3D printing, which involves various methods, materials and equipment, has evolved over the years and has the ability to transform manufacturing and logistics processes. Additive manufacturing has been widely applied in different industries, including construction, prototyping and biomechanical [1, 2]. Recent improvements in 3D printing allow people to print almost any desired product in a short time. Starting from shoes to bigger machining tools can be printed out quickly, which ultimately saves both time and money [3].

### 2. 3D printing technologies that using photopolymer resin

Solid ground curing (SGC) is a photo-polymer-based additive manufacturing (or 3D printing) technology used for producing models, prototypes, patterns, and production parts, in which the production of the layer geometry is carried out by means of a high-powered UV lamp through a mask. As the basis of solid ground curing is the exposure of each layer of the model by means of a lamp through a mask, the processing time for the generation of

a layer is independent of the complexity of the layer. While the method offered good accuracy and a very high fabrication rate, it suffered from high acquisition and operating costs due to system complexity. This led to poor market acceptance. While the company still exists, systems are no longer being sold. Nevertheless, it is still an interesting example of the many technologies other than stereolithography, its predeceasing rapid prototyping process that also utilizes photo-polymer materials [4].

Stereolithography (SLA or SL; also known as stereolithography apparatus, optical fabrication, photo-solidification, or resin printing) is a form of 3D printing technology used for creating models, prototypes, patterns, and production parts in a layer by layer fashion using photopolymerization, a process by which light causes chains of molecules to link, forming polymers. Those polymers then make up the body of a three-dimensional solid. Stereolithography can be used to create things such as prototypes for products in development, medical models, and computer hardware, as well as in many other applications. While stereolithography is fast and can produce almost any design, it can be expensive [5].

Digital Light Processing (DLP) is a similar process to stereolithography in that it is a 3D printing process, which works with photopolymers. The major difference is the light source. DLP uses a more conventional light source, such as an arc lamp with a liquid crystal display panel, which is applied to the entire surface of the vat of photopolymer resin in a single pass, generally making it faster than SL. Also like SL, DLP produces highly accurate parts with excellent resolution, but its similarities also include the same requirements for support structures and post-curing. However, one advantage of DLP over SL is that only a shallow vat of resin is required to facilitate the process, which generally results in less waste and lower running costs [6].

MultiJet Modeling (MJM) is one of the high-end solutions in the 3D printing market. Multi-jet technology ensures the speed of the process, which makes it, fit for manufacturing on an industrial scale. On material side there are various options available like regular photopolymers, waxes, flexible or hard polymers, rubbers, PEG, etc. along with novel materials like water, ceramics, alcohols, etc. [7].

### **3. Photopolymers and process of polymerization**

Photopolymer or light-activated resin is a polymer that changes its properties when exposed to light, often in the ultraviolet or visible region of the electromagnetic spectrum. These changes are often manifested structurally, for example, hardening of the material occurs because of cross-linking when exposed to light.

Types of photopolymers (different forms): some are liquid, while some are in the form of sheet [8]. In the case of 3D printing, photopolymers are typically liquid plastic resins that harden when introduced to a light source, such as a laser, a lamp, a projector or light-emitting diodes (LEDs) [9].

Components of photopolymers: several including binders, photoinitiators, additives, chemical agents, plasticizers and colorants. Three main components, which build the photopolymers, are binders or oligomers, monomers and photoinitiators [3].

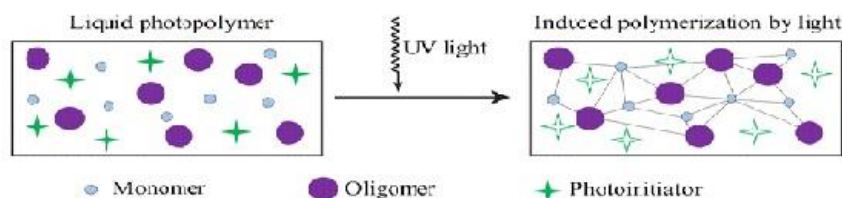


Fig. 1. The process of polymerization [3]

Photopolymers are thermosets, meaning that, once the chemical reaction takes place to harden the material, it cannot be remelted [9].

The properties of a photocured material, such as flexibility, adhesion, and chemical resistance are provided by the functionalized oligomers present in the photocurable composite. Oligomers are typically epoxides, urethanes, polyethers, or polyesters, each of which provides specific properties to the resulting material. Each of these oligomers is typically functionalized by an acrylate. Acrylated urethane oligomers are typically abrasion resistant, tough, and flexible making ideal coatings for floors, paper, printing plates, and packaging materials. Acrylated polyethers and polyesters result in very hard solvent resistant films, however, polyethers are prone to UV degradation and therefore are rarely used in UV curable material. Often formulations are composed of several types of oligomers to achieve the desirable properties for a material. The monomers used in radiation curable systems help control the speed of cure, crosslink density, final surface properties of the film, and viscosity of the resin. Examples of monomers include styrene, N-vinylpyrrolidone, and acrylates. Like oligomers, several types of monomers can be employed to achieve the desirable properties of the final material [8].

#### 4. Polymer composites with high mechanical performance and excellent functionality

3D printing of polymer composites solves these problems by combining the matrix and reinforcements to achieve a system with more useful structural or functional properties non-attainable by any of the constituent alone. Incorporation of particle, fiber or nanomaterial reinforcements into polymers permits the fabrication of polymer matrix composites, which are characterized by high mechanical performance and excellent functionality [10].

Fiber reinforced polymer (FRP) composites are an essential class of structural materials for the aerospace, automotive, marine, and infrastructure industries due to their excellent strength-to-weight ratio, stiffness-to-weight ratio, and durability. Although the incorporation of high aspect carbon nanofillers (nanotubes, nanoparticles, nanoplates, and nanofibers) into polymer composites can significantly improve the modulus, strength, and fracture toughness of the composite [11].

The discovery of graphene and graphene-based polymer nanocomposites is a significant addition in the area of nanoscience, so playing an important role in modern science and technology. Graphene with high electrical, thermal and mechanical properties is quite important as nanofiller in polymer matrices for extraordinary performance materials [12].

Graphene and its derivatives can be applied via incorporation of fully exfoliated graphene oxide (GO) or reduced GO nanosheets into the polymeric matrix: GO can be well dispersed, particularly in hydrophilic polymers.

Novel graphene-based polymer composites are emerging as a new class of highly functional advanced materials that hold promise for a more versatile and cheaper alternative, for example, to carbon nanotubes-based composites. The technique of UV-curing was applied to produce graphene/polymers composites both with acrylates (by radical polymerization), and epoxides (by cationic way) obtaining nanocomposites with improved mechanical and electrical properties [13].

Blending graphene with polymers by methods of traditional composites can only improve a little bit of mechanical properties; however, it usually greatly decreases the composites electrical conductivities due to the low content of graphene in resultant composites. Recently, graphene oxide (GO), a derivate of graphene, possessing excellent mechanical properties, become an ideal candidate for assembling high performance graphene-based nanocomposites due to their abundant functional groups [14].

### 5. Strength of materials

Strength of materials, also called mechanics of materials, is a subject that deals with the behavior of solid objects subject to stresses and strains.

The study of strength of materials often refers to various methods of calculating the stresses and strains in structural members. The methods employed to predict the response of a structure under loading and its susceptibility to various failure modes takes into account the properties of the materials such as its yield strength, ultimate strength, Young's modulus, and Poisson's ratio; in addition the mechanical element's macroscopic properties (geometric properties), such as its length, width, thickness, boundary constraints and abrupt changes in geometry such as holes are considered.

Uniaxial stress is expressed by  $F/A$ , where  $F$  is the force [N] acting on an area  $A$  [ $m^2$ ].

Compressive stress (or compression) is the stress state caused by an applied load that acts to reduce the length of the material (compression member) along the axis of the applied load; it is in other words a stress state that causes a squeezing of the material. A simple case of compression is the uniaxial compression induced by the action of opposite, pushing forces.

Tensile stress is the stress state caused by an applied load that tends to elongate the material along the axis of the applied load, in other words the stress caused by pulling the material. The strength of structures of equal cross sectional area loaded in tension is independent of shape of the cross section.

Shear stress is the stress state caused by the combined energy of a pair of opposing forces acting along parallel lines of action through the material, in other words the stress caused by faces of the material sliding relative to one another. An example is cutting paper with scissors or stresses due to torsional loading.

Strain (deformation) is the change in geometry created when stress is applied (because of applied forces, gravitational fields, accelerations, thermal expansion, etc.). Deformation is express by the displacement field of the material.

A material's strength is dependent on its microstructure. The engineering processes to which a material is subjected can alter this microstructure. The variety of strengthening mechanisms that alter the strength of a material includes work hardening, solid solution

strengthening, precipitation hardening, and grain boundary strengthening and can be explained quantitatively and qualitatively. Strengthening mechanisms are accompanied by the caveat that some other mechanical properties of the material may degenerate in an attempt to make the material stronger.

Strength is expressed in terms of the limiting values of the compressive stress, tensile stress, and shear stresses that would cause failure. The effects of dynamic loading are probably the most important practical consideration of the strength of materials, especially the problem of fatigue [15].

### **6. Experimental part**

The samples of composites GO/photopolymer resin was prepared by method of solution intercalation. Nanocomposites with 0.1 wt. %, 0.5 wt. %, and 1 wt. % GO were prepared by dispersed flakes GO in acetone ( chloroform) solution (100 ml) in an ultrasonic bath ~ 1 h for approximately to obtain an organic GO dispersion. The dimensions of GO: three types used – D1, D10 and D50, with lateral dimensions 0.05 to 1 µm; 1 to 10 µm and 10 to 50 µm respectively. The photopolymer resin was added to the resulting solution in the form of a suspension and sonicated for another 2 h. After that, the acetone was evaporated by heating and stirring by a Teflon-coated magnetic stir for 12 h at 70 °C (chloroform was evaporated by heating and stirring for 18 h at 95 °C) for the removal of the organic solvents. The resulting mixture was transferred to the resin tank of the SLA 3D printer after a short time of cooling under room temperature. The 3D structures were achieved via a bottom-up SLA approach. The as-prepared printed structure was wash in an isopropanol solution for a few minutes in order to remove the residual resin on the product surface. Mild annealing was carried out in a vacuum oven at 50 °C and 100 °C for 12 hours. The length of the sample is 35 mm, thickness is 2 µm.

### **7. Results and Discussion**

The aim of our work is design of photopolymer resin for 3D printing with outstanding mechanical properties.

3D printing of polymer composites solves these problems by combining the matrix and reinforcements to achieve a system with more useful structural or functional properties non attainable by any of the constituent alone. Incorporation of particle, fibre or nanomaterial reinforcements into polymers permits the fabrication of polymer matrix composites, which are characterized by high mechanical performance and excellent functionality [10].

Fibre reinforced polymer (FRP) composites are an essential class of structural materials for the aerospace, automotive, marine, and infrastructure industries due to their excellent strength-to-weight ratio, stiffness-to-weight ratio, and durability [11].

Recently, graphene oxide (GO), a derivate of graphene, possessing excellent mechanical properties, become an ideal candidate for assembling high performance graphene-based nanocomposites due to their abundant functional groups [14].

In order to be effective at low addition levels GO it is critical that the graphene is present in single or few layers with no agglomeration. Graphene oxide dispersed easy into single sheets in polar solvents as the ideal way of achieving this during compounding.

The single graphene sheet (Fig. 2) has superior mechanical properties, however, the mechanical properties of pure collective graphene products or graphene composites are usually significantly compromise by the weak inter-sheet interaction. Therefore, at present there remains a major challenge regarding how to strengthen the interactions between the adjacent graphene sheets or the interaction between graphene sheet and its modifiers. The functionalization of graphene with conjugated organic molecules provides a handle for improving mechanical and thermal properties as well as tuning the optical properties [16].

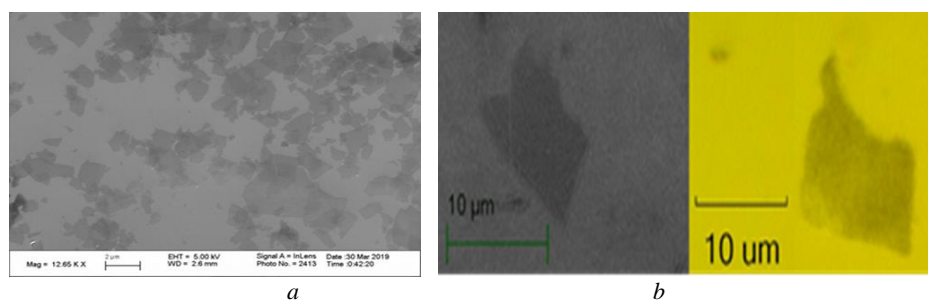


Fig. 2. SEM images of single-layer flakes of graphene oxide (GO):  
(a) scale 2  $\mu\text{m}$ , (b) scale 10  $\mu\text{m}$

In our investigation, we used Prima Creator photopolymer resin is a high-quality resin made from the best materials with high mechanical properties and single-layer flakes of graphene oxide (Table 1). The dimensions of GO: three types used – D1, D10 and D50, with lateral dimensions 0.05 to 1  $\mu\text{m}$ ; 1 to 10  $\mu\text{m}$  and 10 to 50  $\mu\text{m}$  respectively. The samples of composites GO/photopolymer resin with 0.1 wt. %, 0.5 wt. %, and 1 wt. % GO was prepared by method of solution intercalation. The 3D structure was obtained via a bottom-up SLA approach (Fig. 3).

Table 1

Photopolymer resin for 3d printing

Photopolymer resin				
Brand	Wanhao (China)	PrimaCreator (Sweden)	Zortrax (Poland)	Hurz Labs (Russia)
Price 1L	59.00 €	59.90 €	129.80 €	123 €
Hardness	75 Shore D	85–88 Shore D	88 Shore D	87–92 Shore D
Tensile strength	21.4 MPa (horizontal direction) 15.2 MPa (vertical direction)	42.0 MPa	36–52 MPa	45 MPa
Flexural Strength	5.57 MPa (vertical direction)	60 MPa	59–70 MPa	–
Bending strength	8.43 MPa (horizontal direction)	–	–	–
Elongation at break(Strain)	6 %	10 %	11–20 %	4–6 %

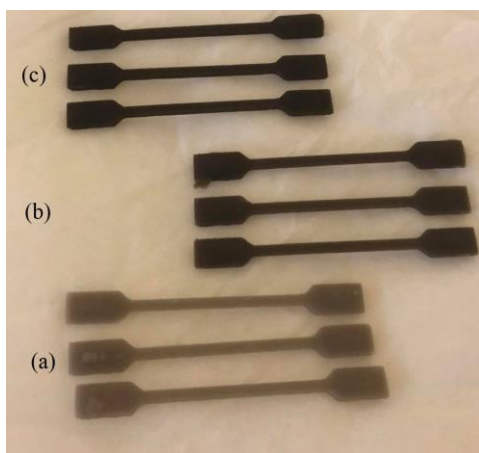


Fig. 3. The samples of composites GO/photopolymer resin with (a) 0.1 wt. % GO; (b) 0.5 wt. % GO; (c) 1 wt. % GO

The general trend observed – decrease in tensile strength (UTS) with an increase in GO concentration (Table 2, fig. 4), can be explained by the fact that at higher GO concentrations, the nanosheets tend to aggregate, which decreases cross-link sites and disrupt the polymer chain orientations at high strain values.

Table 2

Ultimate tensile strength (UTS) and the content of GO, wt. %

Ultimate tensile strength (UTS), MPa	wt. % graphene oxide
6.61	0
6.61	0.1
6.40	0.5
6.26	1.0

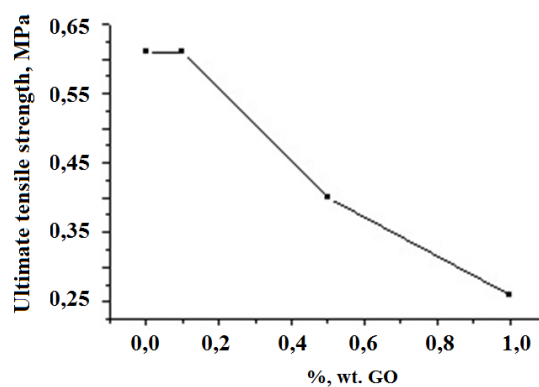


Fig. 4. The dependence of the ultimate tensile strength from the content of GO, wt. %

The high degree of agglomeration in the 3D printed GO sample leads to an interruption of photo-curing, resulting in a decrease in photo-crosslinking.

The presence of GO in the resin can lower the efficiency of photopolymerization because the filler can serve as a barrier or hindrance to incoming laser light. GO is acting as a chain transfer agent, which inhibits the further growth of polymer chain.

We can be employed certain post-processing steps to alleviate this problem. For instance, Manapat et al. [17] enhanced thermomechanical properties of SLA fabricated GO nanocomposites via a simple mild annealing process (100 °C for 12 h), which resulted in drastic increase in mechanical properties with the highest percent increase recorded at 673.6 % for the 1 wt. % GO nanocomposites. The assumptions used to explain these phenomena, were verified through spectroscopic techniques by Manapat et al. and can be summed up as follows: (1) There is lower defect density with increasing annealing temperature; (2) There is enhanced cross-linking between GO and the resin at 100 °C due to acid-catalyzed, esterification, and (3) the sample lost intercalated water in its structure at 100 °C and hence no mass loss was observed in this region.

GO-resin interaction may affect the viscosity of the matrix, which is an important consideration to ensure good quality of SLA-printed parts. Moreover, the resin must be curable and have a proper cured depth. Transparency must be enough to allow the curing of a whole layer. In practice, the resin should have a viscosity less than 5 Pa·s (5 000 mP·s) to be used for SLA. The surface functionalization of GO before adding to photosensitive resin can improve dispersibility and interfacial compatibility of GO nanosheets with the photosensitive resin.

## 8. Conclusion

Therefore, polymer composites for 3D printing, which are formed based on photopolymer resin and GO, have been studied and obtained. We observed – decrease in tensile strength (UTS) with an increase in GO concentration. This can be explained by the fact that at higher GO concentrations, the nanosheets tend to aggregate and disrupt the polymer chain orientations at high strain values. The presence of GO in the resin can lower the efficiency of photopolymerization because the filler can serve as a barrier or hindrance to incoming laser light. That problem can be solved by surface functionalization of GO before adding to photosensitive resin. That can improve dispersibility and interfacial compatibility of GO nanosheets with the photosensitive resin.

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**ПОЛІМЕРНІ КОМПОЗИТИ ДЛЯ 3D ДРУКУ****Н. Ощাপовська<sup>1</sup>, В. Дутка<sup>1</sup>, В. Храновський<sup>2</sup>**<sup>1</sup>*Львівський національний університет імені Івана Франка,  
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Тривимірний (3D) друк – це унікальна технологія, яка дає змогу виготовляти складні конструкції за короткий період часу з мінімальною витратою матеріалу. Використання пластмас та інших полімерів стає все більш поширеним у нашому суспільстві. Від автомобілів і харчових упаковок до захисних покриттів, застосування полімерів постійно збільшується, що потребує збільшення функціональності та продуктивності.

Сьогодні велику увагу привертає графен оксид (GO) як матеріал наповнювача, що використовують для армування полімерних композитів. Ми отримали та дослідили полімерні композити за допомогою 3D друку, які сформовані на основі фотополімерної смоли та неорганічного наповнювача оксиду графену. Такі полімерні композити володіють більш корисними структурними або функціональними властивостями. Включення частинок, волокон або наноматеріальних армувань у полімери дає можливість виготовляти композити полімерних матриць, які характеризуються високими механічними характеристиками та чудовою функціональністю. Армовані полімерні композити є важливим класом конструкційних матеріалів для аерокосмічної, автомобільної, морської та інфраструктурної галузей завдяки прекрасному співвідношенню міцності та жорсткості до ваги та довговічності. Зразки композитів GO/фотополімерна смола з вмістом 0,1 мас. %, 0,5 мас. % та 1 мас. % GO отримано методом інтеркаляції з розчину. Виготовлення тривимірної структури досягнуто за допомогою методу цифрової обробки світла (DLP). Простежується зниження міцності на розрив (UTS) зі збільшенням концентрації GO, що пояснюють агрегацією GO. Вирішити цю проблему можна шляхом функціоналізації поверхні GO перед додаванням до світлочутливої фотополімерної смоли, що покращить сумісність між поверхнями нанопластів GO з фоточутливою смолою.

*Ключові слова:* 3D друк, полімерні композити, оксид графену, фотополімерна смола, армування.

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