Microstructural Investigations of 3D Printed Reinforcing Network in Recycled Silicone Rubber Composites

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Abstract. Recycled silicone rubber has grown interest due to its excellent mechanic properties, obtained at favorable production costs, which are supported by the use of already available materials waste. Here, we have used three different 3D printed polymeric networks (photopolymerizing resin (SLA), hard photopolymerizing resin (SLA) and Polyethylene terephthalate glycol (PETG)) to reinforce a matrix of recicled silicone rubber. The samples were obtained in the form of technical plates consisting of the 3D networks and additive material. These were introduced in the molten base material consisting of 60% liquid silicone rubber (binder) and 40% recycled silicone rubber powder. The micro- morphology of the resulted samples was investigated through scanning electron microscopy (SEM) using the FEI Nova NanoSEM 630 microscope. The morphological results showed a good binding of the three component phases of the composite materials, with strong interface bonds. This information is an essential premise in obtaining a complete picture concerning the performances of a composite material in its final application.

Keywords: recycled silicone rubber · 3D printing · composite polymer · reinforcing network

1 Introduction

It is known that plastic materials have replaced metals in many industrial applications due to advantages such as diversity of mechanical and chemical properties, which has lead to an increased assortment diversity, reduced energy consumption, easy processing, reuced density, increased chemical resistance, good electrical and thermal insulators, etc. [1].

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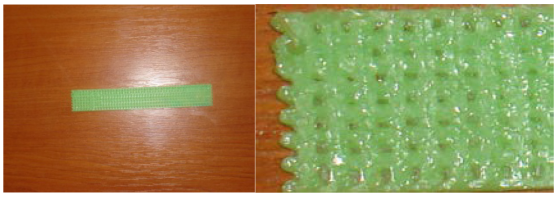

Fig. 1. Sample I macroscopic morphology.

Constitutive basic elements of plastic materials are organic polymers. These are obtained through polymerization from many unsaturated identical molecules which shape a macromolecule [2]. Such materials are silicones which are part of the thermoplastic materials group. They are characterized by extreme stabilty and they can maintain their properties at temperatures higher than the limits of carbon-based polymers. Other properties of silicones are the intert character and resistance to oxidation. Due to increased costs, the production volume is low in comparison to other plastic materials. Silicone resins have applications in the encapsulation of electronic components in aerospatial application, due to their electrical resistance and dielectric properties, being used at temperatures up to 300 °C.

The importance of silicone rubbers is mainly given by the advantage that they can preserve their elastic behaviour in a broad range of temperatures, maintaining their flexibility at temperatures down to -80 °C [3, 4]. The applications of silicone rubbers count cable insulation, hydraulic systems gaskets, door and hatches of planes, etc.

The recycled silicone rubber is obtained through specific technologies and due to its properties is the most stable currently available recycled polymer. It showes a particular fiability combined with an increased usage period, advantages obtained at favorable production costs. Recycled silicone rubbers have the best time- resistance ratio, in both normal and extreme conditions [5].

The applications of silicone rubber have been long known in precision engineering and medical applications. Due to the cheap obtaining technologies, recovered silicone rubber benefits from dynamic properties at least as good as the original material [6]. Our group has recently proved that through the addition of organic natural materials (filtered eggshells, snailshells and shells powders) into the matrix of recovered silicone rubber results varied compositions of nanostructured composite materials with different applications [7].

Due to the various use of recycled silicone rubber, many research studies have undergone in order to improve the material hardness and elasticity [8]. In this regards, a series of network structured materials were obtained through 3D printing.

2 Materials and Methods

Sample I is a photopolymerizing resin (SLA), a liquid plastic material which was hardened through the exposure to an UV fascicle with smooth texture. Its increased flexibility properties determine the final products to be pliable and resistant to impact. It shows the following morphology (see Fig. 1) and mechanical characteristics presented in Table 1.

Table 1. Sample I mechanic properties. [4]

Traction properties	Before hardening	After hardening
Tensile strength	29.8 MPa	61.5 MPa
Young module	13.0 GPa	27.0 GPa
Elongation at break	20%	5%
Bending properties		
Bending module	0.97 GPa	2.38 GPa
Thermal properties		
Heat deflection temperature 66 psi	52 °C	75 °C

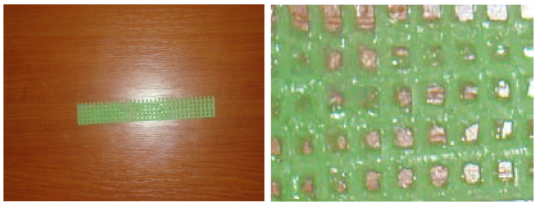

Fig. 2. Sample II macroscopic morphology.

Table 2. Sample II mechanic properties. [4]

Traction properties	After hardening
Tensile strength	41.3 MPa
Young module	210.0 GPa
Elongation at break	31%
Bending properties	
Bending module	1.16 GPa
Thermal properties	
Heat deflection temperature 66 psi	43.2 °C

Sample II is a hard photopolymerizing resin (SLA), based on the transparent turquoise color. It is resilient, can be deformed by applying pressure, but does not crack and returns to its original form. The mechanical characteristics of sample II are given in Table 2.

Table 3. Sample III mechanic properties. [4]

Traction properties	After hardening
Tensile strength	50 MPa
Young module	211.0 GPa
Elongation at break	23%
Bending properties	
Bending module	2020 MPa
Thermal properties	
Heat deflection temperature 66 psi	70 °C

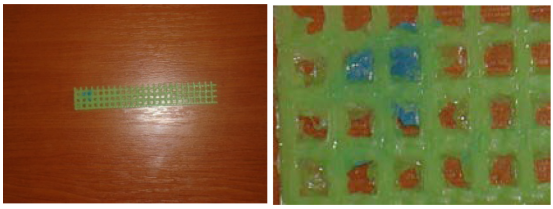

Fig. 3. Sample III macroscopic morphology

Sample III is a thermoplastic material obtained using Fused Deposition Melting technology through successive deposition of melted plastic additive material. When heated becomes malleable and when cooled down it hardens. It is a type of Polyethylene terephthalate glycol (PETG), a polyester with very high hardness and higher impact resistance compared to Acrylonitrile butadiene styrene (ABS) and Polylactic acid (PLA) (Fig. 1).It is flexible, translucent and it is used in case of food containers, electrical and electronic products, structural parts (Fig. 2).

The technical plates from which the samples were made in the form of bars, having the dimensions of 60x8x2,5 mm are composed of 6 samples of type I, II, III additive material. They were introduced into the melt and then cooled based material, which consisted of 60% liquid silicone rubber and 40% recycled silicone rubber powder. Cooling was done in liquid nitrogen for 40 s.

As it was observed from the analysis of the samples, due to the different degree of elasticity, 2 bars were used, in order to reduce in this way the possibility of some imperfections that occurred when cutting the material in order to form the bars (Fig. 3).

In the following section we will indicate some of the most representative sections of material constituted by the addition of networks of additive material.

The metallization of the surfaces was done with a 7 nm thick Au layer, for which the Neva EDV 500 vacuum coating system was used. For the morphological characterization of the samples, we used the FEI Nova NanoSEM 630 field emission scanning electron microscope. [9, 10].

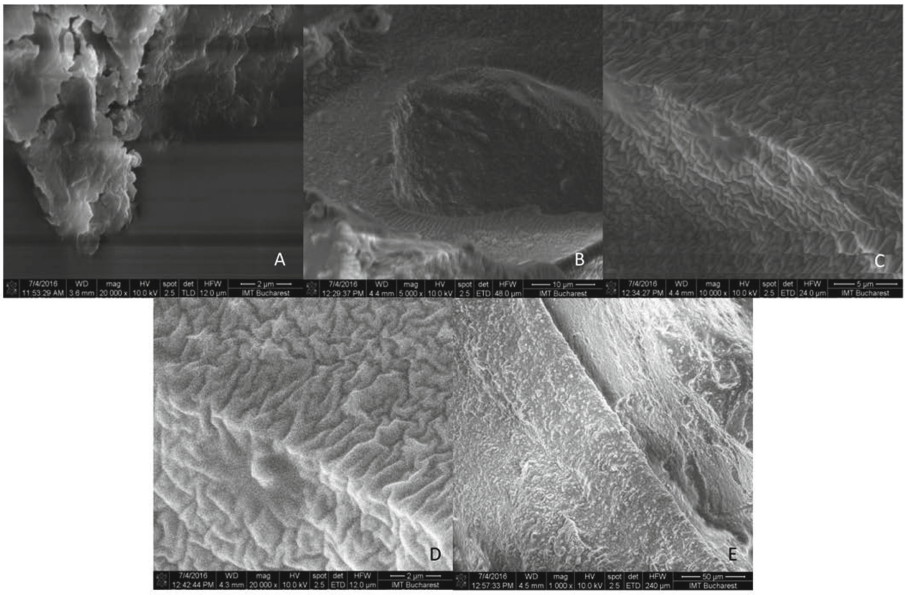

Fig. 4. Sample I microscopic morphology. (A) $h_{inves} = 2\mu m$, optical zoom $2x10^4$; (B) $h_{inves} = 10\mu m$, optical zoom $5x10^4$; (C) $h_{inves} = 5\mu m$, optical zoom $1x10^4$; (D) $h_{inves} = 2\mu m$, optical zoom $2x10^4$; (E) $h_{inves} = 50\mu m$, optical zoom $1x10^3$;

3 Results and Discussion

From the analysis of the structure of the material containing sample I, the material sections that are in the following microphotographs were highlighted, Fig. 4.

There is an appearance of cluster type structures (Fig. 4 A), craters with dimensions of 12–15 μm and depths of 10 μm (Fig. 4 B), but also the appearance of separation zones between the structure of the basic material added with sample I and of the initial material (Fig. 4 C) and at more pronounced investigation dimensions, $h_{inves} = 2\mu m$, optical zoom $= 2x10^4$ (Fig. 4 D). These separation surfaces are accompanied by areas of convolution in opposite directions (Fig. 4 D), but also approximately smooth areas inside the additive structure (Fig. 4 E). Figure 4B emphasized the interface between a recycled silicone grain and the liquid rubber added as a binder in the composition. Figure 4 E showcases the interface between the rubber matrix and the reinforcement polymer network. One can clearly see a strong bond between the component phases.

For the material containing sample III, the following microphotographs were chosen: Fig. 5.

In the case of the structure of the material containing sample II, the surface areas in the following microphotographs were highlighted. In this case, we have large areas with an approximately smooth appearance with rare inclusions determined in the cooling process. (Fig. 5 A). At an in-depth evaluation, they are combined with cavities of material, concentrated more in the center and less at the periphery of the surfaces of the technical plates (Fig. 5 B), (Fig. 5 C), $h_{inves} = 5$ - $30\mu m$, Optical zoom $= 2x10^3$

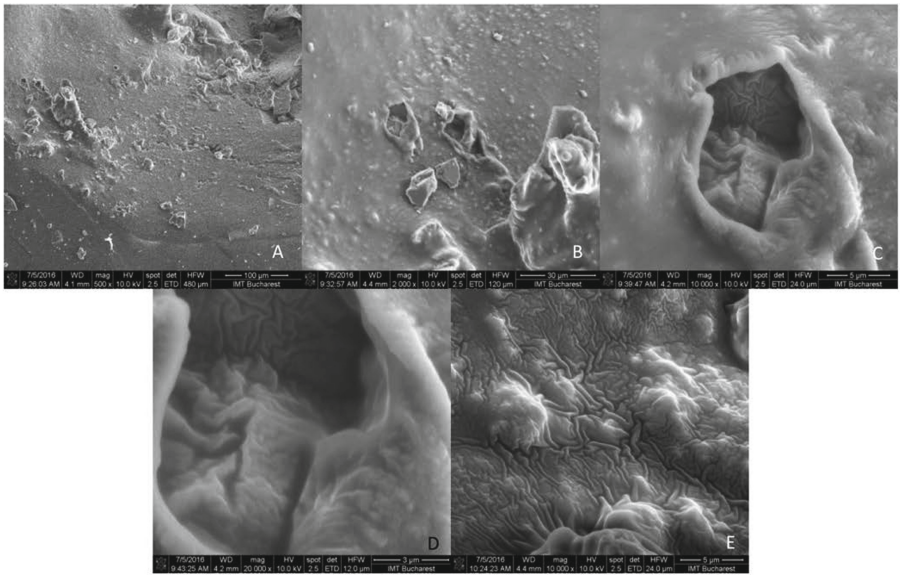

Fig. 5. Sample II microscopic morphology: (A) $h_{inves} = 100\mu m$, optical zoom $5x10^2$; (B) $h_{inves} = 30\mu m$, optical zoom $2x10^3$; (C) $h_{inves} = 5\mu m$, optical zoom $1x10^4$; (D) $h_{inves} = 3\mu m$, optical zoom $2x10^4$; (E) $h_{inves} = 10\mu m$, optical zoom $5x10^3$;

- $1x10^4$. Correspondingly Fig. 5 D, can be clearly observed inside the cavities, a clear area of separation between two surfaces characterized by convolutions of different sizes, arranged in different angular directions at the intersection between the surface of the base material and the additive sample II. Otherwise, we have combinations of inclusions and fine reticular surfaces, a sign of an inhomogeneity of the casting materials. (Fig. 5 E). Inclusions of recycled silicone rubber powder are evidenced in Fig. 5 A, B.

For the material containing sample III following the analysis, the following microphotographs were chosen: Fig. 6.

Here the appearance of the surface is mostly smooth, but in the rare cavities (Fig. 6 A), one can find a varied relief (Fig. 6 B), (Fig. 6 C), where combinations of inclusions and striations appear (Fig. 6 D), $h_{inves} = 30\mu m$, optical zoom $= 2x10^3$. When passing from one slope to another slope of the internal material structure, light reticular areas in a linear or curved direction can be observed. They record the difference in depth between these "peaks", $h_{inves} = 10\mu m$, for optical zoom $= 5x10^3$, (Fig. 6 E), (Fig. 6 F). Inclusions of the recycled silicone rubber powder are showcased in Fig. 6 A. Figures 6 B, C emphasize the tight interface between the reinforcing material and the silicone rubber matrix.

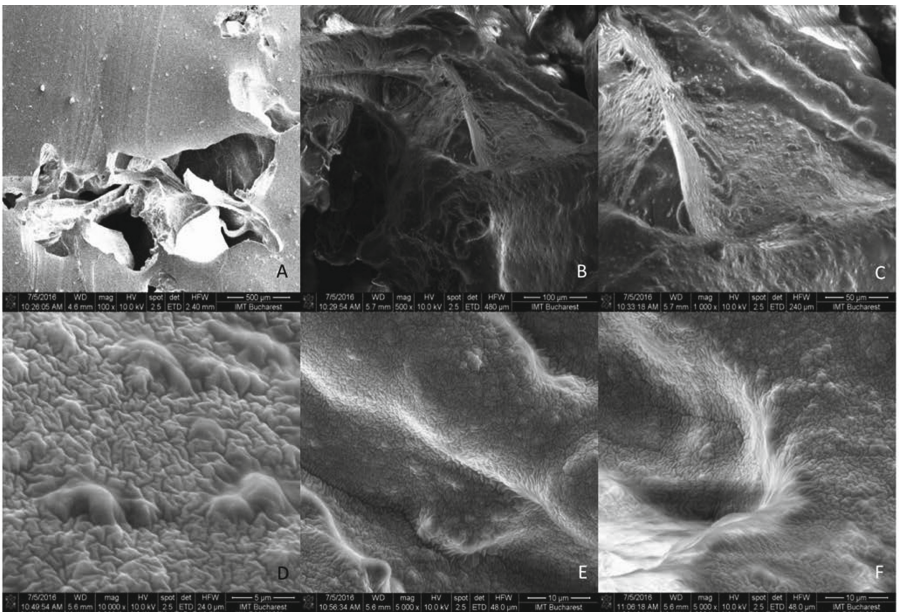

Fig. 6. Sample III microscopic morphology: (A) $h_{inves} = 100\mu m$, optical zoom $5x10^2$; (B) $h_{inves} = 30\mu m$, optical zoom $2x10^3$; (C) $h_{inves} = 100\mu m$, optical zoom $5x10^2$; (D) $h_{inves} = 30\mu m$, optical zoom $2x10^3$; (E) $h_{inves} = 10\mu m$, optical zoom $5x10^3$; (F) $h_{inves} = 10\mu m$, optical zoom $5x10^3$;

4 Conclusion

We have used three different 3D printed polymeric networks fabricated of liquid photopolymerizing resin (SLA), hard photopolymerizing resin (SLA) and respectively of Polyethylene terephthalate glycol (PETG), in order to reinforce a matrix of recicled silicone rubber, where liquid silicone rubber was used as binder. We investigated the micromorphology of the resulted samples using scanning electron microscopy. Our observations showed a good binding of the three component phases, with strong interface bonds.

High resolution morphological investigations enable the determination of possible inhomogenities, imperfections or inclusions in the structure of any of the component phases. This is an important step in creating the premises in corelating and improving basic mechanical characteristics, such as tensile strength, elongation at break and hardness, in the end to obtain a complete picture of the materials' performances in their final application.

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