Nonconventional Technologies Review
Romania, March, 2024

NON-CONVENTIONAL POLYMERIC MATERIAL OF THE LATEST GENERATION FOR STRUCTURAL APPLICATIONS IN CONSTRUCTION

Lucian Paunescu[1], Marius Florin Dragoescu[2] and Bogdan Valentin Paunescu[3]
[1] Daily Sourcing & Research SRL Bucharest, Romania, lucianpaunescu16@gmail.com
[2] National University of Science and Technology POLITEHNICA, Faculty of Applied Chemistry and Material Science, Research Center for Environmental Protection and Eco-Friendly Technologies, Bucharest, Romania, mar_dmf@yahoo.com
[3] Consitrans SA Bucharest, Romania, pnscbogdan@yahoo.com

ABSTRACT: Thermoset polymer composite was made in an original version less expensive than the known techniques, in which alumina-borosilicate glass recycled from used laboratory glass was chosen as filler into the mixture of starting materials together with polyurethane resin as a matrix. The matrix/filler weight ratio was modified during the experiment from 0.67 to 1.22 and this change influenced the features of manufactured products. The temperature and time of the thermoset polymer curing process played an important role. It was opted for the electric heating of the material mixture up to 300-305 ℃ with the heating rate between 3.06-3.22 ℃/min, keeping at the maximum temperature for 100 min, and cooling in about 30 min. Results showed making a dense material type with relatively low heat conductivity. Tensile strength was around 40 MPa and compressive modulus of elasticity registered around 19 GPa, above the level of thermoplastic polymer.

KEYWORDS: thermoset polymer, composite, polyurethane resin, alumina-borosilicate glass, filler.

1. INTRODUCTION

Composite is a material resulted from the use of two or more components with clearly different chemical and physical properties and whose preparation leads to the creation of a material with modified properties, far superior than either of these components. Typically, composite materials include reinforced concrete, wood-based composites, reinforced plastics such as fiber-reinforced polymers or fiberglass, ceramic composites, metal composites, and other advanced composites [1].

According to [2], the future of composite materials in terms of their industrial application is very promising. The automobile and aerospace industries are at the top of the list of economic sectors interested in composites. Lighter and at the same time recyclable construction variants are constantly being developed lately without disturbing their bearing capabilities.

Also called "reactive materials", smart composites are applied in various industries, often using thermosetting plastics or thermoplastics as part of their matrix. They have the ability to choose properties such as heat resistance, resistance to the attack of chemical compounds and aggressive climatic weather by selecting the appropriate material of the matrix.

The ability to manufacture lightweight composites is essential for several industries. Sectors such as aerospace, transport, and infrastructure are extremely interested in this physical feature of composites. Lightweight composites are durable, strong, easy to handle and install.

Bio-composite is the term used for composite materials that contain at least one naturally derived material. It can be included in the basic matrix, in the reinforcement phase or in both. In particular, in infrastructure and constructions, bio-composites can offer alternatives to non-renewable conventional synthetic materials. Bio composites still face some problems such as moisture resistance, thermal instability, poor electrical properties, etc.

Innovation in the field of composite materials is an ongoing process. New manufacturing technologies have the ability to radically transform the world industry through the implementation of advanced techniques [2].

The current work is focused on the production of composites for the construction sector highlighting their effect in this field.

Composite materials were used in construction hundreds of years ago in the form of clay mixed with straw, horsehair plaster, etc. Natural polymer composites appeared at the beginning of the 20th century with the discovery of thermostable resins. Currently, materials with thermostable composite matrices are applied in constructions due to their excellent characteristics: low density, protection against corrosion and environmental agents, excellent mechanical characteristics, heat resistance, durability, transparency to electromagnetic waves (microwaves), electrical insulating properties, relatively low costs. Composites with reinforcing fiber material are applied to window and door frames, secondary structures such as wall panels, roof, floor as well as primary structures for modular constructions. Also, composites with reinforcing fibers represent a very requested material in the bridge infrastructure as well as coverings for buildings to improve their external appearance [3].

Polymer composite is a product obtained by the combination of polymer resins such as polyester, vinyl ester, and epoxy with fillers and reinforcing fibers in order to manufacture a bulk material with superior properties. High-strength fibers of glass, aramid or carbon can be utilized, while the polymer resin has the role to protect the fibers and binds them into a structural mass. Recently, fiber composite materials have become much more interesting for structural load-bearing applications in the construction sector and have been noted as a viable solution for the modernization or rehabilitation of existing civil constructions as a substitute for steel in reinforced concrete and less so for new civil structures. However, it should be mentioned that fiber composite materials are expansive [4].

As noted above, polymer composites are composed of two parts: the reinforcement and the matrix. The polymer contained in the composite acts as a matrix resin, which penetrates the reinforcement bundles, binding them [5].

Resin-based composite turns from an initial plastic phase into a semi-solid phase through the so-called polymerization process. The initiation of the process involves chemical reactions that generate free radicals as a result of the effect of thermal or light energy as well as chemical activation [6].

According to a review on polymer composite peculiarities [7], composite materials are usually called reinforcement arrangements (or fillers), which are incorporated into a matrix. The role of the matrix is to facilitate the cohesion and orientation of the load and to take over the stresses to which the composite is subjected. The products obtained are very heterogeneous and often anisotropic. The composite properties can be determined by the type of matrix and load, the load proportion, the characteristics of the interface, and the peculiarities of the manufacturing process. The composite material is usually composed of one or more discontinuous phases (reinforcements) distributed into a continuous phase (matrix). The introduction of reinforcements with good tensile strength into a polymer matrix leads to the improvement of mechanical and thermal properties. Depending on the type of matrix, composite materials can be organic, mineral and metallic. Organic composites include carbon, laminated tires, and reinforced plastics (resins and short fibers). The main conclusion of the paper [7] was that thermosetting composite materials exhibited exceptional mechanical strength and thermal resistance at high temperature.

According to the work [8], in general, composites are using in infrastructure applications such as buildings, bridges, and roads. The strength and stiffness of composite materials are their major properties. Thermosetting polymer composites have numerous applications in construction, replacing more traditional materials. Usually, they are used in structural applications, where high strength and stiffness are required for resistance to high loads.

By exposure to heat, thermosetting polymer composites tend to increase their thermal resistance without deformation or with slight deformation, but only at higher temperatures compared to thermoplastic materials [9].

2. MATERIALS AND METHODS

2.1 Materials

Polymers forming the network, called thermosets, are the following: epoxy, unsaturated polyester, phenolic, isocyanate, polyurethane, and many others. Unlike thermoplastics, making thermosets is characterized by the chemical reactions that occur, so that the polymer can become crosslinked and can be fixed. It no longer dissolves and no longer flows. Thermal activation is the most frequently used, while hardening with fibers or fillers ensures reducing the shrinkage and improving physical and mechanical properties. The solution chosen in this work was the use of alumina-borosilicate glass as a filler. This filler type is an inexpensive and original fiberglass replica. The glass obtained from recycling the used laboratory glass contains 60-70 % SiO_2, 15-17 % B_2O_3, 7-9 % Al_2O_3, 1-2 % Na_2O and has high temperature resistance. Among the thermoset resin types, polyurethane resin (QXM-7) originally from China was adopted, constituting the matrix. This is widely used in the automobile industry, biomaterials, and construction. Polyurethane is synthesized by the reaction of isocyanate with polyester-based diol, followed by the chain extension reaction for the formation of macromolecules [10].

Four experimental versions of the material mixture composition according to Table 1 were designed.

Table 1. Material composition of thermoset polymer specimens

Material composition	Version (wt. %)			
	No. 1	No. 2	No. 3	No. 4
Polyurethane resin QXM-7	40	45	50	55
Alumina-borosilicate glass (filler)	60	55	50	45

2.2 Methods

The method of thermoset polymer composite production adopted by the authors involved the deposition of fluid resin and reinforcement (fillers) through the free opening of the mould, allowing the composite to be treated. At the operation beginning, a release agent (polyvinyl alcohol) was applied to the inner surface of the metal mould, followed by the application of a coating gel using a brush.

Thermosetting polymer composite processing takes place in several stages. In the first stage, known as "resole stage", the resin is in an insoluble state and a fusible condition. In the second stage, the resin becomes partially soluble and tends to exhibit similar features to thermoplastics, where the changes are reversible. The temporary state of the thermosetting composite lasts only a few minutes in a melted state. In this time interval, the material begins to form cross-links as the temperature increases. In the third stage, the cross-linking reaction takes place in the polymer mass. The final structure of the thermosetting polymer composite is now made. This stage is similar to that of moulding, where the polymers are under pressure and temperature control. The final production of the network structure consists of many cross-linked polymer chains. After the polymer has formed, it can no longer be thermally deformed, remaining stable.

The temperature and duration of curing the thermoset polymer have an important role in the process of determining the network topology and conversion degree. In the manufacturing process presented in the paper, the duration of heating to 300-305 °C was between 87-90 min, followed by keeping the temperature at the maximum value for 100 min and cooling in 30 min. The heating rate starting from the ambient temperature was between 3.06-3.22 °C/min, while the cooling rate varied in the range of 9.17-9.33 °C/min.

After mixing the constituents into the metallic mould, this was introduced into a 1.5 kW-laboratory electric heating oven of 60 L volumetric capacity, operating at temperatures up to 500 °C (Figure 1).

Figure 1. Appearance of 1.5 kW-laboratory electric heating oven

2.3 Characteristics investigation of thermoset polymer composite specimens

The investigation of characteristics of thermoset polymer composite specimens included density, tensile strength, compression modulus of elasticity, heat conductivity, and chemical resistance to industrial solvents and corrosion chemicals. The density was measured using the rheology method according to [11]. Tensile strength was determined in accordance with ASTM D638 and ISO 527-1:2019, while for compressive modulus of elasticity ASTM D3410/D3410M-16e1 (2021) [12] was used. The heat conductivity measuring was carried out according to ASTM D5930-09 recommendations. Chemical resistance guide [13] constituted the investigation basis of the resistance of specimens to the effect of chemicals and industrial solvents attack.

3. RESULTS AND DISCUSSION

3.1 Results

The hot manufacturing process of thermoset polymer composite specimens was performed through their treatment in the electric oven mentioned above. The thermal process parameters corresponding to each of the four specimens are shown in Table 2.

Table 2. Operating parameters of manufacturing process

Operating parameter	Version			
	No. 1	No. 2	No. 3	No. 4
Material mixture amount (g)	350	350	350	350
Heating temperature (°C)	300	305	303	305
Heating time (min)	90	88	87	87
Heating rate (°C/min)	3.06	3.18	3.20	3.22
Keeping time (min)	100	100	100	100
Cooling time (min)	30	30	30	30

Cooling rate (°C/min)	9.17	9.33	9.27	9.33

In principle, operating parameters presented in Table 2 were kept within tight limits, with low insignificant variations.

Which influenced more on the appearance specimen surfaces was changing the ratio between the two main components of the starting mixture: the matrix constituted by polyurethane resin and the filler represented by alumina-borosilicate glass. This matrix/filler ratio constantly increased from 0.67 (version 1) to 1.22 (version 4). The surface appearance of specimens shown in Figure 2 has significantly changed starting from the appearance of specimen (a) corresponding to version 1, in which there is remarkable structural homogeneity and reaching samples (c) and (d) corresponding to versions 3 and 4, with a more disordered appearance and obvious decrease of the filler proportion in relation to the matrix.

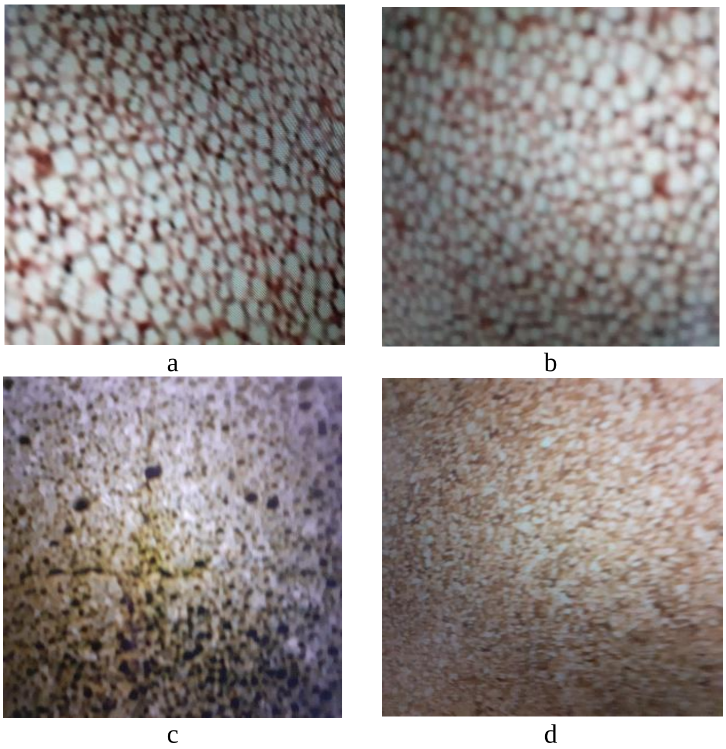
a
b
c
d

Figure 2. Appearance of the surface of thermoset polymer specimens with variable matrix/filler ratio
a – specimen 1; b – specimen 2; c – specimen 3; d – specimen 4.

The influence of the matrix/filler ratio on the quality of thermoset polymer composite specimens was highlighted by determining the physical, mechanical, thermal characteristics as well as the resistance to corrosion attack of chemicals. Table 3 presents these characteristics.

Table 3. Characteristics of thermoset polymer composite

Characteristic	Version			
	No.1	No.2	No.3	No.4
Density (g·cm^{-3})	1.95	1.87	1.74	1.61
Tensile strength (MPa)	38.5	40.2	37.3	38.0
Compression modulus of elasticity (GPa)	19.0	19.3	18.8	18.9
Heat conductivity (W·m^{-3}·K^{-3})	0.29	0.30	0.21	0.16
Resistance to chemical attack (%) of:				
- sodium hypochlorite	89.3	88.9	89.5	89.3
- sodium hydroxide	91.2	90.9	91.4	91.2
- hydrochloric acid	88.0	89.3	88.8	88.6
- acetic acid	90.0	90.2	89.5	89.7
- nitric acid	86.8	87.5	86.9	87.0

Examining the data in Table 3 showed good performances obtained under the conditions of applying the own solution for the filler introduced in the starting mixture, i.e. alumina-borosilicate glass recycled from used laboratory glass.

The first two experimental versions (1 and 2) in which the matrix/filler ratio had values of 0.67 and 0.82, respectively, seem to be the best versions. The products are dense (density of 1.95 and 1.87 g·cm^{-3})

and the thermal conductivity, due to the complex morphology of polymer chains, has acceptably low values (0.29-0.30 $W\cdot m^{-1}\cdot K^{-1}$) to be considered materials with heat-insulating properties. In terms of mechanical strength, tensile resistance measured values are around 40 MPa, which, in the case of a polymer without traditional reinforcing fibers (carbon, steel or glass), constitutes a good performance. Compression modulus of elasticity has also the highest values in versions 1 and 2 (19.0-19.3 GPa) being above the level of thermoplastic polymer composites (around 16 GPa, according to Shah et al., 2021). The results of the chemical attack resistance tests showed excellent values, in all cases the resistance being evaluated above 86.8 %.

The microstructural aspect of experimentally made thermoset polymer specimens is shown in Figure 3.

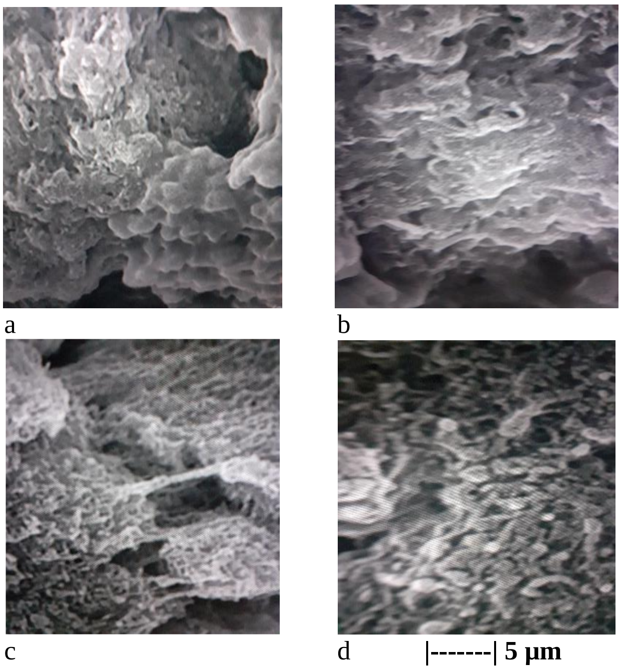

Figure 3. The microstructural aspect of experimentally made thermoset polymer specimens
a – specimen 1; b – specimen 2; c – specimen 3; d – specimen 4.

Practically, the microstructural appearance of the four samples in Figure 3 is not clearly distinguished due to their dense and relatively compact character.

3.2 Discussion

The most common thermoset structure composite is constituted by resin systems. More than 95 % of the thermoset polymer is based on polyester and epoxy resins. However, the experiment described in this work started from the idea of using a less applied polymer resin. Thus, polyurethane resin was chosen. As mentioned above, a crosslinked and rigid thermoset polyurethane is obtained by combining poly-isocyanates with polyols.

On the other hand, the choice of a less expensive material as filler (recycled alumina-borosilicate glass) and generally, rarely used, represented the main element of the work originality.

The combination between polyurethane resin as a matrix and alumina-borosilicate glass as a filler offered the possibility of determining the set of characteristics of polymer composite as well as the opportunity of its use in structural applications in construction.

The best experimental versions were identified after investigating the specimen characteristics, being versions 1 and 2, in which the ratios between matrix and filler were 40/60 and 45/55, respectively.

4. CONCLUSION

Production of thermoset polymer composite in an original version less expensive was the work objective. The choice of polyurethane resin as matrix and recycled alumina-borosilicate glass as filler allowed obtaining a composite with excellent mechanical properties (tensile strength up to 40.2 MPa and compression modulus of elasticity around 19 GPa), thermal resistance, acceptable heat conductivity between 0.16-9.30 $W\cdot m^{-1}\cdot K^{-1}$, and resistance to chemical materials over 86 %, suitable for structural applications in construction. The technical solution adopted by the authors has the advantage to be less expensive than known polymer composites due to the adoption of alumina-borosilicate glass waste.

5. REFERENCES

1. *Composite types*, University of New South Wales, Sydney, Australia, (2023). https://www.unsw.edu.au/science/our-schools/materials/engage-with-us/high-school-students-and-teachers/online-tutorials/composite/composite-types
2. *Composite future trends: The future of composite materials & applications*, Piran Advanced Composites, Wadebridge, UK, (2023). https://pirancomposites.com/composite-future-trends
3. *The composites which revolutionised the construction sector*, Technological Institute of Plastics-AIMPLAS, Valencia, Spain, (2023). https://www.aimplas.net/blog/the-composites-which-revolutionised-the-construction-sector

4. Humphreys, M.F., The use of polymer composites in construction, Queensland University of Technology, Brisbane City, Australia, (2023).
5. Afzal, A., Nawab, Y., Polymer composites, in *Composite Solution for Ballistics*, Woodhead Publishing Series in Composites Science and Engineering, Nawab, Y., Sapuan, S.M., Shaker, K. (eds.), (2021).
6. Al Shaafi, M.M., Factors affecting polymerization of resin-based composites: A literature review, *Saudi Dent Journal*, Elsevier, vol. 29, no. 2, pp. 48-58, (2017). https://doi,org/10.1016/j,sdentj.2017.01.002
7. Hsissou, R., Seghiri, R., Benzekri, Z., Hilali, M., Rafik, M., Elharfi, A., Polymer composite materials: A comprehensive review, *Composite Structures*, Elsevier, vol. 262, (2021). https://doi.org/j.compstruct.2021.113640
8. Dwivedi, U.K., Kumari, N., Foundation of composites, in *Advances in Biomedical Polymers and Composites-Materials and Applications*, Elsevier, Pal, K., Verma, S., Datta, P. (eds.), pp. 31-60, (2023).
9. Sastri, V.R., Materials used in medical devices, in *Plastics in Medical Devices: Properties, Requirements, and Applications*, 3th Edition. William Andrew Applied Science Publishers, Elsevier, Plastic Design Library, Norwich, New York, the United States, pp. 41-64, (2022). https://doi.org/10.1016/B978-0-323-85126-8.00015-1
10. Kausar, A., Role of thermosetting polymer in structural composite, *American Journal of Polymer Science & Engineering*, Ivy Union Publishing, vol. 5, no. 1, pp. 1-12, (2017).
11. Chen, T.T., *Quantifying polymer crosslinking density using rheology and DMA*, Waters Corporation-TA Instruments, New Castle, Delaware, the United States, (2009). https://www.tainstrument.com/applications-notes/quantifying-polymer-crosslinking-density-using-rheology-and-dma/
12. Shah, S.Z.H., Megat-Yusuff, P.S.M., Karuppanan, S., Choudhry, R.S., Din, I.U., Othman, A.R., Sharp, K., Gerard, P., Compression and buckling after impact response of resin-infused thermoplastic and thermoset 3D woven composites, *Composites Part B: Engineering*, Elsevier, vol. 207, (2021). https://doi.org/19,1016/j.compositesb.2020.108592
13. *Chemical resistance guide*, Chemline Plastics, pp. 3-6, Thornhill, Canada, (2015). https://everythinginsidethefence.com/wp-content/uploads/chemline_chemical_resistance_guide)_2015.pdf