

Mechanical Properties of PMMA and PLA Modified Epoxy **Resins**

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Abstract: Last years research in polymers registered an increase of interest regarding polymer mixtures aiming to obtain materials with properties of the mixed polymers. In this respect many studies are pointing the mixtures between a thermoset polymer and a thermoplastic polymer. It is known the fact that thermoplastic polymers are much more malleable than the thermoset ones and the goal is to obtain a mixture with the general properties of the thermoset polymer and with a machining ability proper to the thermoset polymer. The vitrimers are this type of polymers and, some of them, can be obtained by mixing polymers form the two categories. This study is about using solutions of two thermoset polymers to modify the basic properties of three epoxy resins. The results show that the presence of PMMA, respectively, PLA inside the epoxy resin matrix determines changes of the mechanical properties of the formed materials. Without analysing the adhesive properties of new materials is hard to decide about their value from the composites applications point of view.

Keywords: epoxy resins, PMMA, toluene, PLA, chloroform, tensile tests, compressive tests, three point bending tests

1. Introduction

Epoxy resins are largely spread in various applications, starting with small domestic objects, and ending with composites of high-tech industry. They are extremely stable thermoset polymers with outstanding properties and they have a large usage palette covering, unlike other thermoset polymer, coating, casting, impregnating, moulding, and laminating. The chemical formulation of each available epoxy resin is secret and the only known aspect is given by the presence of bisphenol A in each formulation. The PMMA is very well-known thermoplastic polymer used both in 3D printing and protection panels due its transparency comparable with the glass transparency. The PLA is intensively used for 3D printing due its relative low processing temperature, unlike the PMMA, is opaque but can be easily coloured using compatible colorants.

Epoxy resins are most commonly used for making composite structures and protective coatings, knowing that they are substances with extraordinary chemical resistance. Beyond the known models for describing (or predicting) the properties of composite materials, there are currently subject, mainly due to the increase in computing power, of studies that refer to the modelling of the properties of epoxy resins starting from the atomic level, passing through molecular dynamics, and reaching the macroscopic level. Having such a model it would be easier to determine which other polymer would appropriate to change the epoxy resin properties and which is the exact amount of this polymer in the final product.

In [1], the authors synthesized organosilicon additive-modified epoxy resin RSN-6018 through the condensation reaction between organosilicon intermediate (RSN-6018) and epoxy resin (E-20). The results of mechanical property testing showed that the incorporation of RSN-6018 organosilicon improved the hardness of the cured RE films.

Apriany Saludung and his collaborators [2] incorporated epoxy resin into the geopolymer matrix. The improvement of the mechanical strengths and alkaline binding properties of naturally hardened geopolymers by adding epoxy resin can lead to the extensive applications of geopolymer binder in the

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construction industry. In [3], researchers created a high-performance permeable concrete with polyester and epoxy resins. Based on the results of the testing, it was found that using epoxy resin instead of polyester resin and increasing the coarseness of the aggregate decreased the compressive, tensile, and flexural strengths, respectively.

In [4], the authors performed an experimental study on the mechanical behaviour of two polyurethane resins used for geotechnical applications. According to experimental studies, resin density and confining pressure are strongly connected, and given certain restrictions, the mechanical response is constant for the same type of resin. While it was discovered that fracture energy density appeared to depend exclusively on resin type, ultimate stress and Young's modulus were also shown to be dependent on resin density. In particular, an exponential relationship was found between ultimate stress and resin density and between Young's modulus and resin density. The average mechanical behaviour of the various types of resin was discovered to be unaffected by their microstructure, despite the fact that a few specimens exhibited some degree of structural anisotropy.

Elahe Adibzadeh and his co-workers [5] created self-healing epoxy layers and double-layer microcapsules with benzoyl peroxide and vinyl ester resin. For this purpose, bilayer gelatine-gum-Arabic/urea-formaldehyde (Gel-GA/PUF) microcapsules containing either benzoyl peroxide (BPO) or vinyl ester resin (VER) were prepared separately in a two-stage synthesis approach.

In [6], researchers designed a composite material consisting of polyurethane and epoxy resin with a multi-level structure and high performance. The DA interaction between the maleimide group in linear polyurethane and the furan group in linear epoxy resin produced the reversible cross-linking composite material. And this is vitrimer type behaviour. In [7], the authors tested the adhesion of functional layers based on epoxy and polyurethane resins to an aluminium substrate. The polymer coatings were applied to an aluminium substrate after it had been cleaned and/or treated with electro corundum abrasive blasting.

In [8], the authors studied the changes in structure, mechanical, and adhesion properties of vinylester resins after aging. Chemical and structural changes were observed in vinylester resins after aging in a climatic chamber. In this work, vinylester resins are post-cured during different aging cycles (where they are aged at high temperatures and variable relative humidity). The first three days are when most changes happen. Between 25 and 140°C during heat treatment, mechanical characteristics are reduced. However, at a temperature close to Tg, no changes in mechanical properties occur as aging time increases. Furthermore, aging reduces the shear strength of shear joints, although mechanical properties are unaffected at temperatures above Tg (i.e., completely cured VE resin).

A. Hajime Kishi and his collaborators [9], investigated the effect of small amounts of curing catalysts on the nanostructures and mechanical properties of epoxy/acrylic block copolymer blends. In [10], a type of solvent-free epoxy-modified silicone resin transparent coating with high transparency and low volume shrinkage was produced. The silicone layers that were obtained have a transmittance greater than 95% and a hardness of 5H after UV curing with a percentage of 3% by mass for 20 s. It is discovered that the silicone produced materials exhibit reasonable volume contraction, good adhesion, and acceptable heat stability.

In [11], the mechanical performance against impact loading of GFR acrylic laminate composites was studied and compared with composites made with epoxy and polyester resins. In addition, different acrylic matrices filled with shock modifiers were prepared to study the improvement of mechanical performance against impact loads. The impact strength of pure modified and unmodified Elium Acrylic resin was shown to be significantly higher than that of pure epoxy or polyester.

Zhigang Li and his collaborators [12], fabricated and mechanically characterized sandwich composites based on polyurethane resins for three-dimensional fabric reinforcement. The 3D fabrics were produced by sewing jute yarns with configurable structures using Kevlar fibre yarns, while an epoxy resin was impregnated into the 3D fabrics, achieving a more uniform distribution of resin and voids and thus a better impregnation of the polyurethane resin for the sandwich composite. The fracture

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surfaces of the composites were analysed by SEM microscopy after they had undergone compression, bending, and impact testing.

In this study [13], a series of BER-modified silicone rubber ablation composites were prepared by melting, mixing, and cold pressing. The ablation resistance of the composites was investigated by ablation tests and characterization for the ablated samples. XRD measurement demonstrated that the ceramization reaction occurred during the ablation process and SiC ceramic was produced.

In [14] is described a successful synthesis of a series of polyurethane-modified epoxy acrylate resins with various caprolactone units to lessen the viscosity of polyurethane-modified epoxy acrylate resins. The influences of the ε-caprolactone unit on the viscosity of the resins and the double bond conversion of the cured films were studied. The thermo-mechanical and dynamic properties, mechanical properties, thermal stability, and base properties of the UV-cured coatings were also evaluated. Yuxuan Wang and Quansheng Liu [15], studied the rheological and mechanical properties of grout modified with water-soluble epoxy resins. From the experimental tests, it was shown that the water-soluble epoxy resin improved the rheological and mechanical properties of the composite mortar. The uniform distribution of the epoxy resin in the composite grout favoured the hydration reaction of the cement.

Qiusheng He et al. [16] evaluated the performance of asphalt modified with polyurethane resin and epoxy resin as an adhesive layer material for steel-UHPC composite bridge pavements. PEA possesses excellent mechanical properties due to the formation of the IPN structure and the hardening effect of asphalt. The high-temperature stability of PEA is much better than the one of SBS-modified asphalt.

M. Sousa and his collaborators [17], carried out a comprehensive experimental study on the effects of hygrothermal aging on GFRP profiles pultruded with two alternative resin matrices -unsaturated polyester (UP) and vinyl ester (VE) - used in civil engineering applications. In all mechanical tests, the VE profile performed better in terms of durability than the UP profile, with decreases in all attributes of less than 10% overall. For both profiles, strength properties were consistently more affected by hygrothermal aging than stiffness properties.

In [18] a pavement mix of epoxy resins was developed. The strength and deformation characteristics of the mixtures were analysed by uniaxial penetration, compression, and bending tests with small beams. The results showed that high-temperature curing can accelerate the strength development in the initial stage of the epoxy resin pavement mixture. In addition, both curing time and the binder-to-aggregate ratio affect the strength and performance of epoxy resin pavement mixtures. Increasing the amount of binder material is beneficial to improve the deformation resistance of the mixture.

Dongzhi Chen et al. [19], studied the thermal behaviour and mechanical properties of new RTV silicone rubbers using divinyl-hexa[(trimethoxysilyl)ethyl]-POSS as a cross-linking agent. The results showed significantly improved effects on thermal stability and mechanical properties compared to PDMS polymer prepared with tetraethoxysilane (TEOS). The observed improvements in thermal properties could be attributed to the effective three-dimensional network structures resulting from the DVPS structure. It was found that the cross-linking agent POSS facilitated the formation of cross-links in the degradation residues.

Jun Park and Min Kim [20], investigated the interfacial bond between epoxy resin coatings and concrete substrates subjected to different exposure conditions. The exposure conditions significantly affected the tensile strength. As the exposure times increased, the tensile strength decreased, except for bisphenol A with cresyl glycidyl ether (BGEI). BGEI showed the highest tensile strength during exposure to tap water (3.78MPa) and seawater (3.66MPa). In contrast to what was seen when exposed to saltwater, tap water penetration decreased the tensile strength following exposure to tap water with the addition of phenolic novolac resin and hexanediol diglycidyl ether.

In [21], the authors analysed the curing kinetics of four epoxy resins using a diamine-terminated polyether as curing agent. It has been shown that a diamine-terminated polyether (DAPE) can enhance the flexibility of epoxy systems, which is attributed to its unique chemical structure. The outcomes demonstrated that the Sestak-Berggren (SB(m,n)) kinetic model can adequately describe the curing reaction and fit the experimental curves.

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In [22], a silicone-epoxy copolymer was prepared by synergizing the o-allylphenol-modified (UC-233) and methoxy-terminated (PMPS-S) silicone methylphenyl intermediate. SEM and DMA revealed that the comb-shaped silicone-epoxy copolymer showed better compatibility due to the pre-chemical grafting reaction. TGA also demonstrated that the comb-shaped silicone-epoxy copolymer's thermal stability had increased while maintaining the good mechanical capabilities of the epoxy resin. TGA-FTIR shows the thermal degradation process that methoxy-terminated methylphenyl silicone intermediate (PMPS-S) and phenyl hydrogen-containing silicone oil (UC-233) could inhibit the degradation of epoxy resin.

In [23], the synthesis and investigation of a new brominated vinyl ester resin are presented. DMA results demonstrate that all resin formulations comprising Br-VER exhibit improved mechanical performance compared to commercial vinyl ester resin. The synthesized Br-GVER has a significantly lower viscosity and a longer lifetime (nine hours versus two hours), which negates the need for an inhibitor when used for applications like resin infusion, according to rheological studies on the resin compositions.

In [24], researchers synthesized and characterized new room-temperature vulcanized (RTV) silicone rubbers using polyhedral oligomer Vinyl-Silsesquioxanes (POSS) derivatives as crosslinking agents. The results showed improved effects of POSS on thermal stability, mechanical properties, and hardness compared to PDMS polymers prepared with the traditional tetra-functional cross linkers TMOS and TEOS. The improvements in thermal properties, mechanical properties, and hardness could be attributed to the synergistic effect of increasing the dimensionality of the cross-linked networks in new RTV silicone rubbers resulting from the special three-dimensional structure of the new POSS cross linkers, plasticizing self-bonds.

In [25], a terpene-modified polysiloxane-based polyurethane was designed to improve poor mechanical properties, obvious hydrophilicity, and low heat resistance. The tensile results showed that the stress of the modified polyurethane film could reach 8.82MPa, which was twice higher that of the unmodified polyurethane film. The TG results showed that the modified polyurethane film still had residues at 600°C. In conclusion, water-based polyurethane performed much better when isobornyl acrylate and polysiloxane were combined, showing that terpene chemicals have enormous potential for enhancing polymer performance.

In [26], the effects of polysiloxane on the thermal conductivity and compressive strength of porous silica ceramics were analysed. The addition of polysiloxane to fumed silica was found to increase the compressive strength from 3.9-11.1 to 10.7-14.5MPa with a minimal increase in thermal conductivity. The specific compressive strengths of insulators with polysiloxane-derived silica as a bonding phase were significantly higher compared to those calculated in previous studies. A high compressive strength (14.5MPa) in combination with a low thermal conductivity was obtained for the sample prepared using fumed silica and 20% polysiloxane at 800°C due to improved MSA and the formation of the silica bonding phase derived from chemically compatible polysiloxane. These results suggest that the proposed lightweight porous silicon ceramics are promising for thermal insulation applications.

In [27], the mechanical and tribological performance of epoxy-SiO₂ nanocomposites was evaluated. In order to obtain a high-quality dispersion of epoxy-SiO₂ nanocomposites, ultrasonic mixing was used and the results revealed that the properties of the epoxy matrix with the introduction of nanoparticles in bending, hardness, and impact resistance, as well as the wear and friction coefficient of the nanocomposite, were significantly reduced by adding 1% (volume ratio) of SiO₂ nanoparticles to the epoxy matrix. The high mechanical properties of epoxy-SiO₂ nanocomposites, together with good abrasion, allow the material to normally replace fibres in composites as a partial or full replacement.

The above presented studies reveal the fact that polymer mixtures are of a large interest for their application in composites industry, buildings, but also on some scientific approaches referring to various ways of human intervention aiming to produce better materials.

As it was said the vitrimers seemed to be the future replacements of thermoset polymers (and not only) and in this regard there were many studies regarding epoxy vitrimers, especially the ones with



vegetal source (soy bean oil) but not only [28-30]. Other studies are looking for self-healing epoxy vitrimers or recyclable epoxy vitrimers (with focus on the vitrimers used to form reinforced composites) solving, in this manner, the problem of epoxy resins high stability that is making their residues non-neutralisable [31-35]

2. Materials and methods

For the present study we choose to realize epoxy resins/PMMA, and epoxy resins/PLA mixtures using solvents to realize the mixture between the epoxy resin and the required thermoset polymer. To solvate the PMMA we choose the toluene and we experimentally determined that the solubility limit is of 40g of PMMA/100mL toluene. In the case of PLA the solvent was chloroform and solubility limit was of 20g of PLA/100mL chloroform.

We used three epoxy resins, denoted as E, R, and S [36-38]. The first one, Epiphen RE4020-DE4020 is a multipurpose resin while the last two are casting epoxy resins. All of them are transparent and result as chemical reactions between the respective resin (the main component) and correspondent hardener (in each case the weight ratio being different). The pot time of each of the three resins is different starting with 45min for E resin, 60 min for R resin, and 6 h for S resin. The R and S resins are based on epoxidized soy bean oil while the E resin is based on mixture of bisphenol A and bisphenol F.

All the three resins are bi-component chemical systems, but it is known the fact that there exist epoxy resins that polymerize at UV exposure. This is the reason we intend to analyse the effect of UV exposure of the moulded samples during the first 30 min after moulding. In this regard we named the materials E, R, and S and we placed N for the natural polymerized samples, and L for UV exposed samples in front of the respective epoxy resin.

The materials were formed as plates of 21mmx21mmx5mm using glass realized from two sheets of glass separated by a rubber gasket. All the mould elements were covered with demoulding agent to facilitate the samples extraction. First, the gasket was fixed, by superficial effect of the demoulding agent, on a sheet of glass, than the mixture was poured into the zone delimited by the gasket, and at the end the second sheet of glass was placed above the gasket. The entire mould was fixed using office paper binders and the polymerization occurred in horizontal position (Figure 1).



Figure 1. Images of filled moulds during polymerization and UV exposure

In order to form the PMMA, and respectively, PLA modified materials we solved PMMA in toluene and PLA in chloroform such as to obtain a concentration of 0.1mol phr for each of thermoplastic polymer and each of epoxy resin. Calculated amounts (equals) of solutions of the two thermoplastic were then mixed together with the main component of each resin and kept under continuous agitation up until the entire amount of solvent vaporized. The process was longer for the PMMA/toluene solution (two weeks) than for PLA/chloroform solution (5 days). At the end, measuring the weight of each pot, the six mixtures thermoplastic polymer/epoxy resin were obtained and they seemed to be stable.

Following the same procedure as in the case of pure epoxy samples we formed modified epoxy resins materials denoted by adding a letter after the epoxy resin symbol. This letter is M for PMMA modified materials, and L for PLA modified materials.



After the plates removal from moulds they were subject of thermal consolidation consisting of 72 h at 80°C using an oven with natural ventilation. The images of the samples are presented in Figure 2.

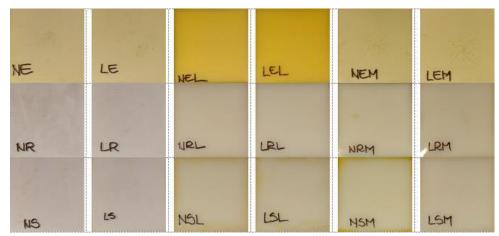


Figure 2. Images of formed plates of materials

After consolidation three samples of each type of mechanical test were cut out from the formed plates using a high pressure water jet machine Figure 3. It was about samples respecting indications of ASTM D638 for tensile tests, and ASTM D790 for three point bending tests. Regarding the compressive tests we decided to use a core drill to cut the samples which were of 8mm diameter and height equal with the plate thickness.

Talking about three samples for each test our study does not qualify as rigorous scientific experimental study, but from the qualitative point of view the number of three samples allows, for each type of test, evaluation of an averaged behaviour and of elastic moduli (three of them – one for each type of test) of materials.

All the mechanical tests were carried out on an *Instron 8802* universal testing machine, using appropriate fixtures (Figure 3) and the soft-ware application *BlueHill*.



Figure 3. Tensile, three point bending, and compressive test fixtures on the *Instron* machine

3. Results and discussions

As it was mentioned above each type of test was realised on three samples of each material and we decided to present the averaged behaviour of each material. The presentation starts with the acquired tensile tests results for all the analysed materials.

In Figure 4 the averaged behaviour of epoxy resin E based materials are presented. In the case of E material it seems that the exposure to the UV radiation has no effect on the tensile response of the material. There is a small difference between the stress and specific elongation at break for the two materials but it might be a consequence of experimental errors (differences in samples thickness, existence of small stress concentrators on the edges of the samples – resulted during cutting). For the EL materials it is noticeable that NEL has a response that is superior to the one of NE (better than the epoxy resin E) but UV exposure reduces the response. In the case of EM materials (the ones modified with PMMA) the situation is inverse – LEM has better response than NEM meaning that UV exposure is beneficial.



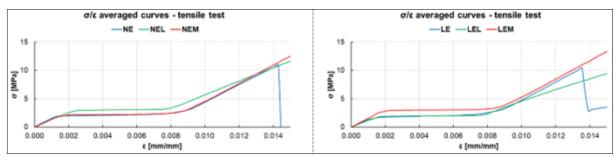


Figure 4. Tensile tests results – epoxy resin E based materials

The tensile results for epoxy resin R based materials are presented in Figure 5. The UV exposure does not affect the basic material and the material modified with PLA but is reducing the behaviour of LRM material with respect to NRM material. Also it is noticeable that the tensile response of NRM and LRM meaning that the epoxy resins R properties are improved by adding PMMA. Also it is noticeable a tinny improvement of tensile response of RL (NRL and LRL) materials with respect to the R (NR and LR) materials.

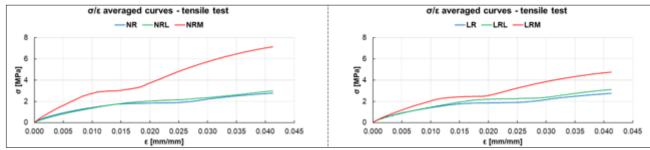


Figure 5. Tensile tests results – epoxy resin R based materials

Regarding the S resin based materials, the tensile tests results are showed in Figure 6. For the epoxy resin S based materials it seems that UV exposure is increasing the tensile response of materials (all of them) but modification of the epoxy resin with PMMA, and respectively PLA leads to a decrease of mechanical response of epoxy resin S (in both situations – with or without UV exposure).

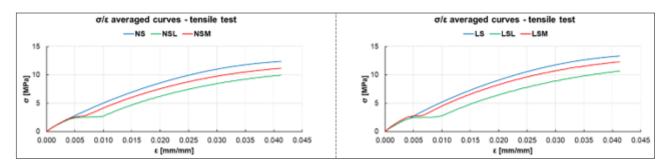


Figure 6. Tensile tests results – epoxy resin S based materials

Analysing together all the three categories of materials it clear that the epoxy resin E returns the best results, followed by epoxy resin S, and finally epoxy resin R.

The bending tests, as well as the tensile tests showed that the epoxy resin E is a fragile one while the other two resins show a plastic behaviour. For the epoxy resin E based materials the results of three point bending tests are given in Figure 7. For the epoxy resin E, as in the case of tensile tests the UV exposure reduces both the stress and the specific deformation at break. For the PMMA modified material the UV exposure does not influence the profile of the averaged curve but it seems that UV exposure turns the



plastic material NEM into a more sensitive material (it breaks on the descendent domain of the stress). PLA modified E epoxy resin is a weak material but after UV exposures it becomes a material.

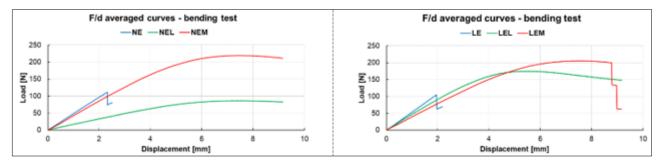


Figure 7. Three point bending tests results – epoxy resin E based materials

For the epoxy resin based materials the results of three point bending tests are presented in Figure 8. With respect to the epoxy resin E materials these materials are weak, they show a short elasticity domain at very low loadings. The best result correspond to LR (epoxy resin R with UV exposure), as in the case of tensile tests confirming that UV exposure is beneficial for the epoxy resin R. The RM materials have the same behaviour with or without UV exposure while for RL material the UV exposure is increasing the bending response.

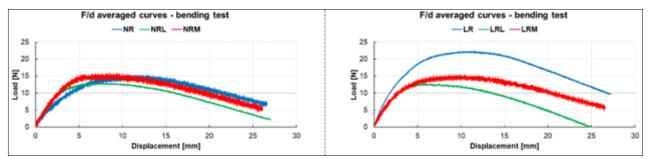


Figure 8. Three point bending tests results – epoxy resin R based materials

In Figure 9 the results of three point bending tests for epoxy resin S based materials are presented. The UV exposure is beneficial for the epoxy resin S (there is an increase in elasticity) while for the two materials formed with PLA, and PMMA respectively, the UV exposure has no effect on maximum load so, practically the UV exposure does not affect the materials.

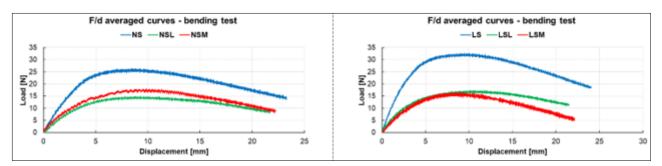


Figure 9. Three point bending tests results – epoxy resin S based materials

For all the performed mechanical tests we set a speed of 5mm/min for the advance of the horizontal console of the testing machine. We used a loading cell with 25kN maximum loading and its precision in force determination is of 2.5N. The data acquisition speed is of 100/s and that produces the effect of trembled line where the reset of force detector is reset.



The compressive tests were performed in nonstandard conditions on small disks of material having the height equal with the material thickness a diameter of 8mm. For homogenous materials, theoretically, the elastic tensile modulus and the elastic compressive modulus should have same value. Performing these tests we just want to verify this assumption. The samples for the compressive tests, as it was said, were extracted from the plates using a core drill and that affected the edge of the samples involving more sources of errors.

The results of compressive tests for epoxy resin E materials are showed in Figure 10. As in the other two types of tests (tensile and three point bending) the epoxy resin E and the material modified with PMMA are not influenced by the UV exposure, and also like in the other two types of tests the PLA modified material exposed to UV (LEL) is better than its correspondent – NEL.

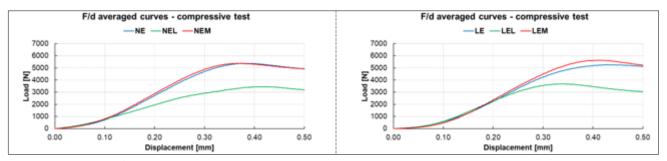


Figure 10. Compressive tests results – epoxy resin E based materials

For the epoxy resin R based materials the results of compressive tests are presented in Figure 11. The trembling aspect of the curves represents a sign that the materials are weak. Once again when exposed to UV the epoxy resin R becomes stronger. In the case of the other two materials RL and RM the compressive tests results show no evidence of any difference between the exposed and unexposed materials.

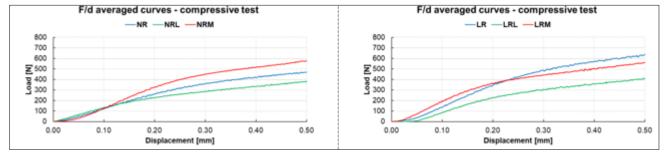


Figure 11. Compressive tests results – epoxy resin R based materials

Finally, in Figure 12 the results of compressive tests for epoxy resin based materials are presented. There are not significant differences between the curves profiles. The UV exposure of all the materials produces a slight improvement of the compressive response. Also the modification of the epoxy resin with each one of the two thermoplastic polymers improves the compressive behaviour of the respective material

A complete image of the mechanical analysis is given in Figures 13 - 15 presenting the values of the three elastic moduli (tensile, bending, and compressive) for all the analysed materials paired such as the difference to be visible. It is obvious that the lowest values of elastic moduli are recorded for compressive tests because of the samples imperfections (irregular edges resulted from the extraction with the core drill).



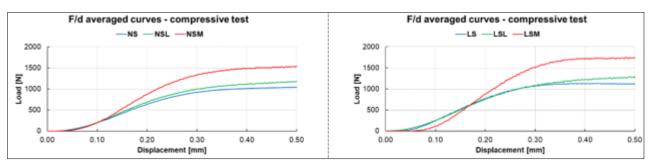


Figure 12. Compressive tests results – epoxy resin S based materials

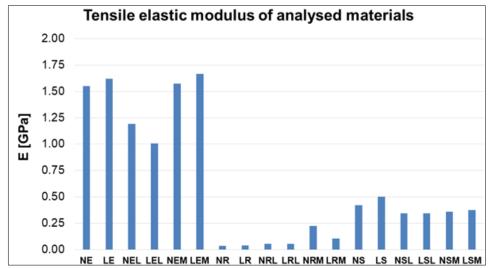


Figure 13. Tensile elastic modulus of each analysed material

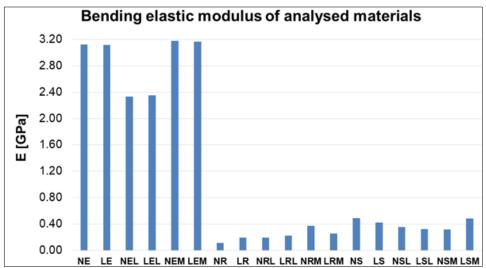


Figure 14. Bending elastic modulus of each analysed material



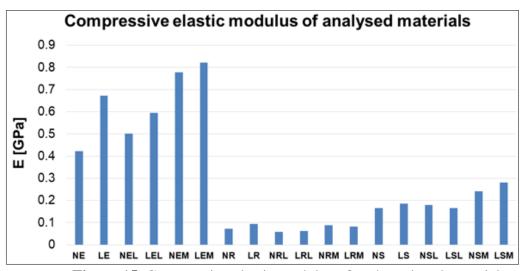


Figure 15. Compressive elastic modulus of each analysed material

4. Conclusions

We analysed the mechanical behaviour of three epoxy resins and of other six materials formed by modifying each epoxy resin with 0.1mol phr PLA, and respectively, PMMA. The two thermoplastic polymers were placed into the epoxy resin main component via its solution into a specific solvent (chloroform for PLA, and respectively, toluene for PMMA). The mixture between each resin main component and the required amount of each solution was homogenized and continuously stirred till the solvent vaporization. The process had duration of 5 days for PLA modified epoxy resins and 2 weeks for PMMA modified epoxy resins. The complete vaporization of the solvent was determined by periodical measurement of pots weight.

The final mixtures were a little bit more viscous than the resins but still liquid and right amounts of these mixtures were mixed together with the necessary amount of respective resin's hardener. For all the formed materials the mixture between thermoset polymer containing resin and its hardener the homogenization time was the same – 15 min. The homogenized mixture (liquid) was poured into moulds realised from two sheets of glass and a rubber gasket all of them covered with a demoulding agent. All the materials in one category were formed mean time – all the resins at once, all the PLA modified resins at once, and all the PMMA modified resins at once to avoid the influence of laboratory conditions (room temperature, atmospheric pressure, and air humidity) on the final properties of formed materials.

The materials were demoulded and then they were thermally consolidated for 72 h at 80°C into a natural ventilation oven. From the consolidated plates samples were cut using a high pressure water jet machine (for tensile and three point bending tests) and a core drill (for compressive tests). For each test three samples were tested and the averaged results were presented above.

The main goal of the study was to identify the effect of thermoplastic polymers presence into the thermoset polymer matrix. From this point of view we noticed positive aspects associated with the PMMA presence into all the three studied epoxy resins, and positive aspects associated with the PLA presence into epoxy resin R.

A second objective of the study was to identify the effect of UV exposure of polymerisable mixtures for 30 min after moulding on mechanical properties of studied epoxy resins. It is known the fact that there are some epoxy chemical formulations that are UV polymerisable (especially used in dentistry). We noticed that the UV exposure has beneficial effects on the mechanical responses of materials.

The changes we standpoint in the above presentation might be influenced by the presence of solvent traces inside the polymer structure, but generally we know the presence of solvents leads to slight reductions of the elastic moduli of thermoset polymers.

It is noticeable the fact that the bending modulus reaches the highest values for the E resin (which is brittle), but also reaches almost the same values for the PMMA modified E epoxy resin (without effect

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of UV exposure). The PMMA modified E resin is not brittle anymore and it might be used to form reinforced composites with better capacity of fibres protection if the adhesion of PMMA modified E is not decreased with respect to the E epoxy resin adhesion.

The other two resins are too weak to form reinforced composites but they could be used to form the core of a laminate composite with improved shock resistance, of course if they are enough adhesive to the fibres.

A further study might take into account larger volume fractions of thermoplastic polymers in thermoset polymers aiming to find rules regarding the variation of mechanical parameters with the volume fraction. Also an analysis of solvents presence shell be done by mixing the solvent with the resin, vaporizing the solvent and forming materials as above.

References

- 1.Z. SHEN, Z. XIA, Y. ZHANG, Characterization and properties of epoxy resin (E-20) modified with silicone intermediate RSN-6018, *Progress in Organic Coatings*, vol. **114**, pp. 115-122, ian. 2018, doi: 10.1016/j.porgcoat.2017.10.014.
- 2.A. SALUDUNG, T. AZEYANAGI, Y. OGAWA, K. KAWAI, Alkali leaching and mechanical performance of epoxy resin-reinforced geopolymer composite, *Materials Letters*, vol. **304**, p. 130663, dec. 2021, doi: 10.1016/j.matlet.2021.130663.
- 3.M. TABATABAEIAN, A. KHALOO, H. KHALOO, An innovative high performance pervious concrete with polyester and epoxy resins, *Construction and Building Materials*, vol. **22**8, p. 116820, dec. 2019, doi: 10.1016/j.conbuildmat.2019.116820.
- 4. R. VALENTINO, E. ROMEO, D. STEVANONI, An experimental study on the mechanical behaviour of two polyurethane resins used for geotechnical applications, *Mechanics of Materials*, vol. **71**, pp. 101–113, apr. 2014, doi: 10.1016/j.mechmat.2014.01.007.
- 5.E. ADIBZADEH, S. M. MIRABEDINI, M. BEHZADNASAB, R. R. FARNOOD, A novel two-component self-healing coating comprising vinyl ester resin-filled microcapsules with prolonged anticorrosion performance, *Progress in Organic Coatings*, vol. **154**, p. 106220, mai 2021, doi: 10.1016/j.porgcoat.2021.106220.
- 6.Y.-J. PENG, X. HE, Q. WU, P.-C. SUN, C.-J. WANG, X.-Z. LIU, A new recyclable crosslinked polymer combined polyurethane and epoxy resin, *Polymer*, vol. **149**, pp. 154–163, aug. 2018, doi: 10.1016/j.polymer.2018.06.082.
- 7.P. MAYER, A. DMITRUK, & J. W. KACZMAR, Adhesion of functional layers based on epoxy and polyurethane resins for aluminum substrate, *International Journal of Adhesion and Adhesives*, vol. **109**, p. 102899, sep. 2021, doi: 10.1016/j.ijadhadh.2021.102899.
- 8.C. ALIA, J. A. JOFRE-RECHE, J. C. SUÁREZ, J. M. ARENAS, J. M. MARTÍN-MARTÍNEZ, Characterization of the chemical structure of vinyl ester resin in a climate chamber under different conditions of degradation, *Polymer Degradation and Stability*, vol. **153**, pp. 88–99, iul. 2018, doi: 10.1016/j.polymdegradstab.2018.04.014.
- 9.H. KISHI, K. YAMADA, J. KIMURA, Control of nanostructures and fracture toughness of epoxy/acrylic block copolymer blends using in situ manipulation of the epoxy matrix reaction type, *Polymer*, vol. **176**, pp. 89–100, aug. 2019, doi: 10.1016/j.polymer.2019.05.024.
- 10. X. YANG, *et al.*, Fabrication of UV-curable solvent-free epoxy modified silicone resin coating with high transparency and low volume shrinkage, *Progress in Organic Coatings*, vol. **129**, pp. 96–100, apr. 2019, doi: 10.1016/j.porgcoat.2019.01.005.
- 11.G. KINVI-DOSSOU, *et al.*, Innovative acrylic thermoplastic composites versus conventional composites: Improving the impact performances, *Composite Structures*, vol. **217**, pp. 1–13, iun. 2019, doi: 10.1016/j.compstruct.2019.02.090.
- 12.Z. LI, X. WEI, Z. GAO, J. XU, P. MA, M. WANG, Manufacturing and mechanical characterisation of polyurethane resin based sandwich composites for three-dimensional fabric reinforcement, *Materials Today Communications*, vol. **24**, p. 101046, sep. 2020, doi: 10.1016/j.mtcomm.2020.101046.



- 13.Z. LIU, Z. CHEN, L. YAN, Y. CHEN, M. LIANG, H. ZOU, Ordered graphitized ceramic layer induced by liquid crystal epoxy resin in silicone rubber composites with enhanced ablation resistance performance, *Materials Chemistry and Physics*, vol. **270**, p. 124823, sep. 2021, doi: 10.1016/j.matchemphys.2021.124823.
- 14.Y. XU, J. LUO, X. LIU, R. LIU, Polyurethane modified epoxy acrylate resins containing ε-caprolactone unit, *Progress in Organic Coatings*, vol. **141**, p. 105543, apr. 2020, doi: 10.1016/j.porgcoat.2020.105543.
- 15. Y. WANG, Q. LIU, Investigation on fundamental properties and chemical characterization of water-soluble epoxy resin modified cement grout, *Construction and Building Materials*, vol. **299**, p. 123877, sep. 2021, doi: 10.1016/j.conbuildmat.2021.123877.
- 16. Q. HE, H. ZHANG, J. LI, H. DUAN, Performance evaluation of polyurethane/epoxy resin modified asphalt as adhesive layer material for steel-UHPC composite bridge deck pavements, *Construction and Building Materials*, vol. **291**, p. 123364, iul. 2021, doi: 10.1016/j.conbuildmat.2021.123364.
- 17. J. M. SOUSA, M. GARRIDO, J. R. CORREIA, S. CABRAL-FONSECA, Hygrothermal agent of pultruded GFRP profiles: Comparative study of unsaturated polyester and vinyl ester resin matrices, *Composites Part A: Applied Science and Manufacturing*, vol. **140**, p. 106193, ian. 2021, doi: 10.1016/j.compositesa.2020.106193.
- 18. J. XU, B. MA, W. MAO, X. WANG, Strength characteristics and prediction of epoxy resin pavement mixture, *Construction and Building Materials*, vol. **283**, p. 122682, mai 2021, doi: 10.1016/j.conbuildmat.2021.122682.
- 19. D. CHEN *et al.*, Thermal behaviour and mechanical properties of novel RTV silicone rubbers using divinyl-hexa[(trimethoxysilyl)ethyl]-POSS as cross-linker, *Polymer Degradation and Stability*, vol. **95**, nr. **4**, pp. 618–626, apr. 2010, <u>doi: 10.1016/j.polymdegradstab.2009.12.002.</u>
- 20. J. K. PARK, M. O. KIM, The effect of different exposure conditions on the pull-off strength of various epoxy resins, *Journal of Building Engineering*, vol. **38**, p. 102223, iun. 2021, doi: 10.1016/j.jobe.2021.102223.
- 21. H. ZHAO, S. XU, A. GUO, J. LI, D. LIU, The Curing Kinetics Analysis of Four Epoxy Resins Using a Diamine Terminated Polyether as Curing Agent, *Thermochimica Acta*, vol. **702**, p. 178987, aug. 2021, doi: 10.1016/j.tca.2021.178987.
- 22. Y. LING, J. LUO, Z. HENG, Y. CHEN, H. ZOU, M. LIANG, Synthesis of a comb-like silicone-epoxy co-polymer with high thermal stability and mechanical properties for ablative materials, *Reactive and Functional Polymers*, vol. **157**, p. 104742, dec. 2020, doi: 10.1016/j.reactfunctpolym.2020.104742.

 23. S. DEV, P. N. SHAH, Y. ZHANG, D. RYAN, C. J. HANSEN, Y. LEE, Synthesis and mechanical properties of flame retardant vinyl ester resin for structural composites, *Polymer*, vol. **133**, pp. 20–29, dec. 2017, doi: 10.1016/j.polymer.2017.11.017.
- 24. D. CHEN, *et al.*, Synthesis and characterization of novel room temperature vulcanized (RTV) silicone rubbers using Vinyl-POSS derivatives as cross linking agents, *Polymer*, vol. **51**, nr. **17**, pp. 3867–3878, aug. 2010, <u>doi: 10.1016/j.polymer.2010.06.028</u>.
- 25. Y. QIAN, F. DONG, L. GUO, X. XU, H. LIU, Two-component waterborne polyurethane modified with terpene derivative-based polysiloxane for coatings via a thiol-ene click reaction, *Industrial Crops and Products*, vol. 171, p. 113903, nov. 2021, doi: 10.1016/j.indcrop.2021.113903.
- 26.S. RAJPOOT, R. MALIK, Y.-W. KIM, Effects of polysiloxane on thermal conductivity and compressive strength of porous silica ceramics, *Ceramics International*, vol. **45**, nr. **17**, pp. 21270–21277, dec. 2019, doi: 10.1016/j.ceramint.2019.07.109.
- 27. K. BHARADWAJA, S. SRINIVASA RAO, T. BABURAO, Epoxy/SiO₂ nanocomposite mechanical properties and tribological performance, *Materials Today: Proceedings*, p. S2214785321078974, dec. 2021, doi: 10.1016/j.matpr.2021.12.172.
- 28.W. CAI, et al., A Multifunctional Biomass Zinc Catalyst for Epoxy-Based Vitrimers and Composites, Eur. Polym. J., vol. 188, p. 111936, Apr. 2023, doi: 10.1016/j.eurpolymj.2023.111936.

https://revmaterialeplastice.ro https://doi.org/10.37358/Mat.Plast.1964



- 29.K. L. CHONG, *et al.*, A review on recent approaches to sustainable bio-based epoxy vitrimer from epoxidized vegetable oils, *Ind. Crops Prod.*, vol. **189**, p. 115857, Dec. 2022, doi: 10.1016/j.indcrop.2022.115857.
- 30.C. LI, B. JU, S. ZHANG, Fully bio-based hydroxy ester vitrimer synthesized by crosslinking epoxidized soybean oil with doubly esterified starch, *Carbohydr. Polym.*, vol. **302**, p. 120442, Feb. 2023, doi: 10.1016/j.carbpol.2022.120442.
- 31.Q.-R. REN, S. GU, J.-H. LIU, Y.-Z. WANG, L. CHEN, Catalyst-free reprocessable, degradable and intrinsically flame-retardant epoxy vitrimer for carbon fiber reinforced composites, *Polym. Degrad. Stab.*, vol. **211**, p. 110315, May 2023, doi: 10.1016/j.polymdegradstab.2023.110315.
- 32.W. ZHANG, *et al.*, Scalable micropatterned epoxy vitrimer films by thermo-triggered bond exchange for repairable and recyclable triboelectric nanogenerators, *Appl. Mater. Today*, vol. **32**, p. 101789, Jun. 2023, doi: 10.1016/j.apmt.2023.101789.
- 33.M. CHEN, W. LUO, S. LIN, B. ZHENG, H. ZHANG, Recyclable, reprocessable, self-healing elastomer-like epoxy vitrimer with low dielectric permittivity and its closed-loop recyclable carbon fiber reinforced composite, *Compos. Part B Eng.*, vol. **257**, p. 110666, May 2023, doi: 10.1016/j.compositesb.2023.110666.
- 34.P. WU, L. LIU, Z. WU, A transesterification-based epoxy vitrimer synthesis enabled high crack self-healing efficiency to fibrous composites, *Compos. Part Appl. Sci. Manuf.*, vol. **162**, p. 107170, Nov. 2022, doi: 10.1016/j.compositesa.2022.107170.
- 35.I. TOENDEPI, S. ZHU, Y. LIU, L. ZHANG, Y. WEI, W. LIU, Synthesis and structure-property relationship of epoxy vitrimers containing different acetal structures, *Polymer*, vol. **272**, p. 125862, Apr. 2023, doi: 10.1016/j.polymer.2023.125862.
- 36. ***http://www.polydis.ro/wp-content/uploads/2014/08/Epiphen-4020.pdf.
- 37. ***https://deve.ro/rasina-epoxidica-transparenta/rasina-epoxidica-de-turnare-rt1919/c/131
- 38. *** https://deve.ro/rasina-epoxidica-transparenta/rasina-epoxidica-de-turnare-sg1452/c/131

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