Enhanced Electric Photoconductivity of Modified Epoxy Resin

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Abstract: The basic idea of this study is based on the hypothesis that it is possible to obtain nanostructures by stimulating local chemical reactions. Starting with this hypothesis we assumed that it is possible to disperse some inorganic agent into the epoxy resin and stimulating the mixtures we could get some nano-structures what are changing the basic electric behaviour of the polymer matrix. We dissolved some metallic chlorides in DMF (dimethylformamide) and we mixed together the solution with the epoxy resin (the main component). Applying various external stimuli we get materials showing various properties, different from the epoxy resin properties. The electric photoconductivity is increased (in some cases) but the mechanical properties are damaged due the solvent presence into the polymer matrix.

Keywords: epoxy resin, inorganic agents, dimethylformamide, electric photoconductivity

1. Introduction

It is known that almost all the usual polymers are electric insulators and that explains their extremely wide application area. Starting with the smallest kitchen tools, passing through sports applications, and ending with applications in automotive industry the low electric and thermal conductivity represent advantages. When it is about polymer matrix composites the low electric conductivity of the polymers reduces the application area due to their ability to accumulate electric charge. This accumulation may lead to accidental discharge with disastrous consequences when these composites are used for application involving reciprocal movement or movement through a potentially charged environment, such as helicopter blades. One solution is to cover the composite part with some conductive film or to use an electric conductive polymer to form the composite.

For the newest applications - the last TV sets generations, the last generations of computers and cell phones and, the photovoltaic panels - the electro conductive polymers represent a sine qua non condition. This is the reason that moves forward the quest for electro conductive polymers or for methods to change the basic properties of a polymer from insulator to electrical conductor.

Between the usual thermoset polymers the epoxy resins are detaching due to their astonishing properties as high thermal stability, high adhesiveness, and excellent mechanical properties. They are also extremely versatile being used for coating, forming, moulding or laminating.

Finding a solution to increase the electric conductivity of such a polymer is the goal that determined this study. We assumed that it is possible to reach the above mentioned goal by placing some inorganic substances into the polymer volume but without changing the other properties of the epoxy resin.

Polymers are widely used in industry and in our daily life due to their diverse functionality, low density, low cost, and excellent chemical stability [1]. Considerable progress has been made in the previous decade in the development of high-performance polymers due to the structure and ionic character of their bonds [2].

Conductive polymers have established themselves in interdisciplinary scientific research regarding the modern aspects of organic synthesis, electrochemistry, catalysis, solid body physics, and thin layer physics, with applications in the field of cutting-edge unconventional technologies. Applied research focused on microelectronics, electrochemistry, catalysis, energy, and information storage due to the

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special properties of these materials and the functions they can perform: transport and storage of electric charges, activation of electrochemical processes, selective permeability, and ion transport [3, 4]. Conductive polymers are organic polymers with high intrinsic electrical conductivities. They received increasing attention with the fundamental contribution of Heeger, Mac Diarmid, and Shirakawa, who jointly received the Nobel Prize in Chemistry in 2000 [5 - 9].

The addition of various conductive nanomaterials to polymer matrices causes some interesting electrical properties in the polymers. The incorporation of graphene nanosheets can provide more possibilities for electron transfer in the nanocomposite, making it electrically conductive [10, 11].

In the research [12], MoS_2-PANI (polyaniline) nanocomposites were made in three different ways, using hydrothermal and in situ polymerization. For the production of MoS_2-PANI composites, the first step was to fabricate a sample by the simple hydrothermal method, adding presynthesized polyaniline nanofibers and MoS_2 to the solution. The second method was through in situ chemical oxidative polymerization of aniline by adding MoS_2 nanopowder to the solution during PANI synthesis. The third way was achieved by the hydrothermal method by adding one-dimensional polyaniline nanofibers to the solution during MoS_2 synthesis.

Nickel oxide (NiO) is a very promising semiconductor material, it possesses a cubic structure and behaves as an antiferromagnetic material [13, 14]. One of the significant applications of nickel oxide is as a pseudocapacitive material. High electrical conductivity and a large specific surface area are the major requirements of a pseudocapacitive material [15]. Thus, in the study [16], NiO nanoparticles were synthesized by the simple sol-gel method, using rice starch as a precursor, at a temperature of 500°C. The DC (direct current) conductivity of pure NiO was improved by incorporating PVP (polyvinyl-pirolydinone)-stabilized PANI. The temperature-dependent conductivity of the NiO-PANI composites was monitored, and the sample with 70% (mass percent) NiO showed the highest conductivity with a value of $2.1129 \cdot 10^{-2} S \cdot cm^{-1}$ at the temperature of 90°C. The conductivity values obtained for NiO-PANI composites are high, they have good thermal stability. These materials can be used for various electrical applications.

Another conductive polymer very often used in research, due to its high conductivity and excellent mechanical properties, is polypyrrole (Ppy) [17, 18]. It is already used as an electrode for rechargeable batteries, as an electromagnetic shield in electronic equipment, in printed circuit boards, and in many other diverse applications [19-23]. One of the important variables for modifying Ppy properties, especially conductivity, is the type of oxidant. The doping process creates a break in the polymer chain and/or transfers electrons to the conducting polymer chain, resulting in positive or negative polarons/ bipolarons [24]. Through this process, Ppy can be oxidized, causing the removal of electrons from the chain, resulting in the formation of the polaron, and further oxidation would remove the second electron from the chain, resulting in the formation of a bipolaron double charge [25]. In order to improve the process mentioned earlier, the authors of the information source [26], succeeded in using sodium molybdate (Na_2MoO_4) to improve the corrosion resistance of steel samples coated with modified Ppy. Conductive polymers modified with Na_2MoO_4 are commonly used to improve the performance of organic coatings and increase their lifetime.

In the paper [27], among others, the electrical performance of the Ppy-EG (expanded graphite) composite was investigated. A worm structure of EG was obtained by a thermal expansion method, and Ppy-EG composites were fabricated from polymerization by a chemical oxidation method. The results showed that the EG foil layers are losing their uniformity and they are presenting many voids in their structure. The average particle dispersion in the Ppy matrix was revealed by SEM (Scanning Electron Microscopy) and XRD (X Ray Diffractometry) examinations. The electrical conductivity reached $108 S \cdot cm^{-1}$. The surface and porous structure of the EG layers (foils) can easily form conductive bridges within the Ppy matrix.

Another polymer that has attracted a lot of attention recently due to its promising conductivity, which can be tuned from insulator to semiconductor and then to the range of metals by doping, is polythiophene (PTh) [28, 29]. PTh was synthesized, in reference [30], by a standard chemical oxidation procedure using

ferric chloride ($FeCl_3$) as the oxidant without any post-doping process. The synthesis procedure was optimized by varying different parameters such as reaction temperature, monomer-to-oxidant ratio, solvent system, reaction time, and oxidant addition time to achieve maximum electrical conductivity without compromising the product. Multi-walled carbon nanotube and polythiophene nanocomposite materials can be used to make polymer light-emitting diodes, electrochemical sensors, supercapacitors, energy storage devices, shielding against electromagnetic radiation, etc. [31 - 34].

Nanoparticles are known to affect several electrical characteristics of conductive polymers. In order to increase electrical conductivity, the paper [35] reports the controlled size and synthesis of poly(p-phenylene) (PPP) nanoparticles using benzene (C_6H_6), aluminum chloride ($AlCl_3$), and copper chloride ($CuCl_2$) as monomers, catalysts, and oxidants, respectively. These particles are then incorporated with a surfactant template. Concentrations of Sorbitan Tristearate (Span65), Polysorbate 80 (Tween80) and TritonX100 as surfactants were investigated. Scanning Electron Microscopy (SEM) images showed various undoped PPPs (uPPPs) in an irregular shape, coral reef shape, spherical shape and worm-like shape with particle sizes between 30 and 120nm.

In comparison to composites reinforced with CNTs or one-dimensional GNPs (unitary composites), hybrid nanocomposites reinforced with two or more materials and of diverse geometric shapes, sizes, and aspect ratios could achieve greater conductivity at a lower cost [36]. These materials with different geometries can affect the formation of the 3D network structure and bring different properties, such as strength and high conductivity, to the nanocomposite [37, 38]. Based on this knowledge, a geometric-analytical 3D Monte Carlo model is used in the study [39] to evaluate the piezoresistivity and electrical conductivity of polymer nanocomposites modified with carbon nanotubes (CNTs)-graphene nano-composites (GNPs). GNPs and CNTs are compared to each other as a narrow cylinder, a solid with random distribution, and a rectangular cube, respectively. The relative resistance and electrical conductivity variations with strain are calculated after creating a random CNT-GNP network.

In the paper [40], an ecological and versatile supercritical carbon dioxide ($scCO_2$) phase super-position method was adopted to enhance the electrical conductivity of composite foams with double-percolated conductive networks. At a multi-walled carbon nanotube (MWCNT) loading of 2% (volume percent) and a thickness of 2mm, the composite foams of polystyrene (PS), poly(methyl methacrylate) and MWCNT (PS-PMMA-MWCNT), with the density of $0.49 g/cm^3$, achieved an electrical conductivity of $2.69 S \cdot cm^{-1}$ and an EMI SE electromagnetic interference shielding efficiency of 25.30dB, already meeting commercial EMI shielding requirements. When the MWCNT content was low, phase thickening of the polymer blends was relatively easy to initiate, resulting in increased phase sizes and reduced interfacial areas. The composite foams exhibited a bimodal cellular structure. The electrical conductivities of solid and porous composites could be greatly improved.

In another study [41], flexible polymer composite films composed of polyaniline (PANI), silver nanoparticles (Ag-NPs) and methylcellulose are fabricated for portable electronic devices. The MC-PANI-Ag composite films are characterized using X-Ray Diffraction (XRD), Scanning Electron Micro-scopy (SEM), transmission electron microscopy (TEM), and Fourier Transformed Infrared spectroscopy (FTIR) techniques. In the study [42], fabricated Ag-Cu nanoparticles were used as conductive fillers and epoxy resin as polymer to produce Ag-Cu epoxy composites. Researchers [43] used chemical polymerization procedures to create a mixture of pure polyaniline (PANI) and barium sulfide ($BaSO_4$) in order to explore the various mechanisms for enhancing the electrical conductivity of polymer composites. Polymerization of aniline in the presence of Ba^{2+} as a seed causes a remarkable change in XRD crystallography, from an amorphous pure PANI pattern to a crystalline orthorhombic pattern. The formation of crystalline PANI causes a change in each of the lattice parameters, particle size, and crystalline deformation of $BaSO_4$.

The study [44] aims to change the conductivity of PMC (polymer matrix composite) by modifying the polymer matrix with different powders. Clay, CNTs, and ferrites were used as fillers, and epoxy Epiphen RE-4020 with Epiphen DE-4020 as a hardener was used as a matrix, and plain-type fabric, realised of alternating untwisted aramid fibres and carbon fibres tows, was used as reinforcement. The

mechanical properties of a PMC are enhanced by the use of reinforcements, so it is natural to ask what happens when a reinforced composite is formed with a loaded polymer matrix. Plates were formed, and their electrical conductivity was evaluated. The concentration of modifying agents was considered, and information was used to form the reinforced composite with the highest conductivity. Using the described forming method, pseudo-laminated composites can be obtained with the outer layers having high conductivity and the core layers having, for example, high magnetic properties. It also seems possible to create a layered material with depth-dependent properties based on the same polymer.

2. Materials and methods
2.1. Materials

We used Yttrium chloride (YCl_3), Barium chloride ($BaCl_2$), and Copper chloride ($CuCl_2$) as inorganic and ionic substances and we dissolved them using dimethylformamide (DMF). The last compound is largely used as plasticizer in plastic materials industry but we tested it and found it able to dissolve the three chlorides. The obtained solution was used to modify the properties of an epoxy resin, namely EPIPHEN RE4020-DE4020 that is a commercial epoxy system with RE4020 the resin and DE4020 the hardener. The resin contains both bisphenol A and bisphenol F and the hardener is a mixture of modified aliphatic amines [45]. All the chemical substances, excepting the epoxy resin, were purchased from *Sigma-Aldrich*. The purity of substances is: higher than 99.8% for DMF, 97% for Copper chloride, and 99.9% for Yttrium chloride hexahydrate, respectively Barium chloride.

Knowing that YBCO (Yttrium Barium Copper Oxide) is a ceramic compound with special properties, another goal of the study was to investigate the possibility of forming YBCO through locally developed chemical reactions (like things happened in the case of gel method to obtain nanostructures). The mixture between resin and hardener (3:1wr) is low exothermic during polymerization and the heat might contribute to formation of ceramic nanostructures.

600mL of DMF were used to dissolve 15.188g of $YCl_3 \cdot H_2O$, 20.823g of $BaCl_2$, and 20.167g of $CuCl_2$. Based on stoichiometry the quantities of inorganic salts were determined such as to enable the $YBa_2Cu_3O_x$ compound formation. The mixture between DMF and the inorganic salts was stirred (using a magnetic stirrer, 1350rot/min, 65°C) on a first stage for 30 days, and other 20 days on a second stage (75rot/min, 70°C) to ensure the solutions homogeneity.

During the study design we established the fact that we need two cylindrical samples to test the electric properties of materials and two plates (250mmx20mmx5mm) to get the samples for the mechanical tests. The necessary amount of liquid mixture to fill the moulds was estimated at 500mL. The samples were realised accordingly to the information presented in Table 1.

Table 1. The materials formation programme

RE4020	DMF solution	DE4020	Special treatment	Material	Volume ratio – vr
382mL	25mL	119mL	-	11	0.10
339mL	50mL	113mL	-	21	0.15
321mL	75mL	107mL	-	31	0.20
382mL	25mL	119mL	SEF1+SEF2	12	0.10
339mL	50mL	113mL	SEF1+SEF2	22	0.15
321mL	75mL	107mL	SEF1+SEF2	32	0.20
382mL	25mL	119mL	SEF1+SEF2+SEF3+SEF4	13	0.10
339mL	50mL	113mL	SEF1+SEF2+SEF3+SEF4	23	0.15
321mL	75mL	107mL	SEF1+SEF2+SEF3+SEF4	33	0.20

After 50 days the solution of chlorides into DMF was homogeneous and the materials formation was started. For the first three materials (11, 21, 31) the necessary amount of resin and solution were mixed together for 5min using a mechanical mixer. The required amount of hardener was then added and the mixture was mixed (using the same mechanical mixer) for 10min. The homogeneous mixture was poured into the moulds that has been closed and left for 7days to polymerize.

The remained volume of solution was exposed to a Sinusoidal Electric Field (SEF) using graphite electrodes (30min, I=50mA – SEF1). The solution was than stirred (1500rot/min, 50°C) for seven days. Prior the formation of next three materials (21, 22, 23) the solution was again exposed to the sinusoidal electric field (SEF2 – 30min, I=100mA) and then the procedure was similar to that described at the formation of first materials.

Again, the remained volume of DMF solution was exposed to the sinusoidal electric field (SEF3 – 60min, I=400mA) then it was stirred for 7 days (1500rot/min, 50°C). Before the last materials formation (31, 32, 33) the DMF solution volume was exposed to the sinusoidal electric field (SEF4 – 90min, I=400mA) and the procedure was followed as in the case of first three materials.

We thought that into the solution the metallic ions and chloride ions might be influenced by an electric field and they could form some different stable structures. In fact the sinusoidal electric field (50Hz) might determine just small oscillations of the ions together with detachment of some carbon atoms from the electrodes.

The materials were removed form moulds, and they were thermally consolidated following a programme recommended by the EPIPHEN producer – 8 h at 60°C, 2h at 80°C, and 1h at 90°C.

The samples required for testing were the cylindrical samples (h=200mm, d=8mm) for the analysis of the electric properties. The plates of materials were cut using a high pressure water jet machine to get the necessary samples for tensile and three point bending tests.

2.2. Methods

Since the epoxy resin is an insulator we measured its electric resistance using a TeraOhm-meter, generally used to determine insulators electric resistance (*Metrel*). The measurements are realised at high voltage (5000V) and to protect both the operator and the apparatus they are done using a ground electrode (guard electrode) - the green wire in Figure 1 and two hot electrodes (red and black wires). We set the entire measurement fixture such as to determine the electric resistance of small part of the sample by placing the hot electrodes at 10mm distance. So, we measured the electric resistance of cylinder of 10mm length and 8mm diameter.

Figure 1. Electrodes placement during the electric resistance measurements

Once the electric resistance measured, we evaluated the electric conductivity using the very well known relation $\sigma = l/RS$, where l is the sample length (the distance between measuring electrodes), S is the area of the transverse section of the sample, and R is the measured electric resistance.

At the first stage the electric conductivity of materials was determined for darkness conditions (without electromagnetic waves exposure) the obtained value is represented as the first point on the curves. Using batteries of ten LEDs the materials were exposed to various wavelengths and the electric resistance was measured as function of electromagnetic radiation wavelength (34 values of the wavelength), and subsequently the electric conductivity was determined.

The mechanical tests (both tensile and three point bending) were performed on standard samples ASTM D638 for tensile tests, and ASTM D790 for three point bending tests on a universal testing machine (*Instron 8002*). For each type of test five samples of each material were tested.

3. Results and discussions

The electric resistance of the epoxy resin was measured in the same conditions as the above described and the results regarding electric photoconductivity are presented in Figure 2. The value of the parameter is of 10^{-11} magnitude order and represents an insulator material. For the other materials the same analysis leads to the results presented in Figures 3 - 5 based on the criterion of the amount of solution used to modify the basic properties of epoxy resin (first digit on the material code) and then on the criterion of the duration of the preparation of the solution (the second digit).
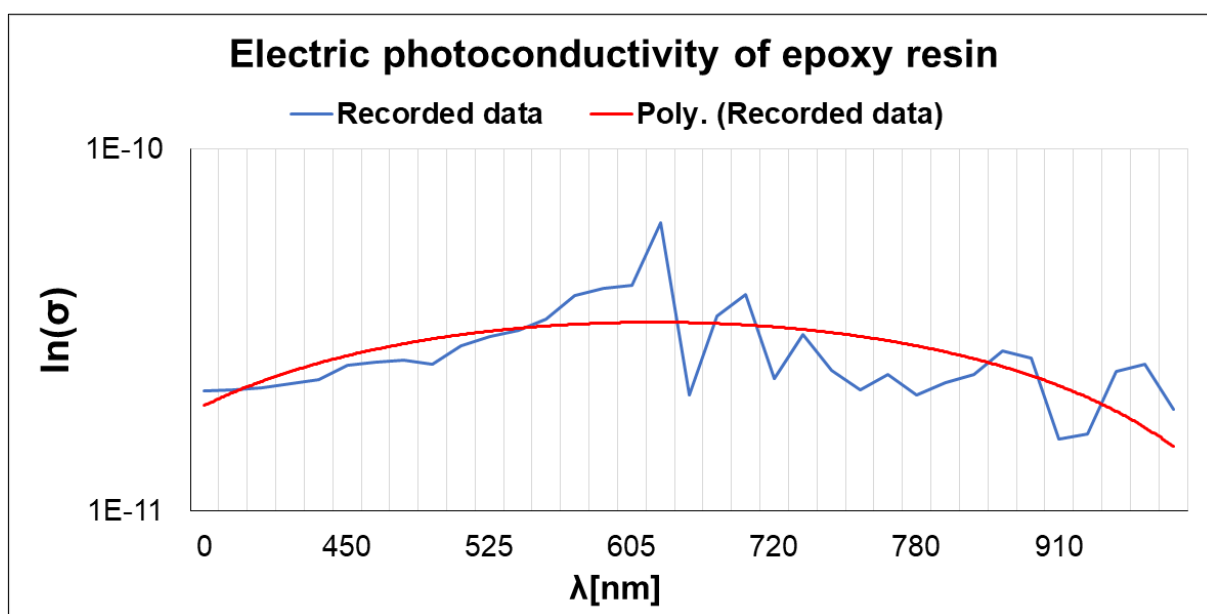
Figure 2. Electric photoconductivity of epoxy resin samples
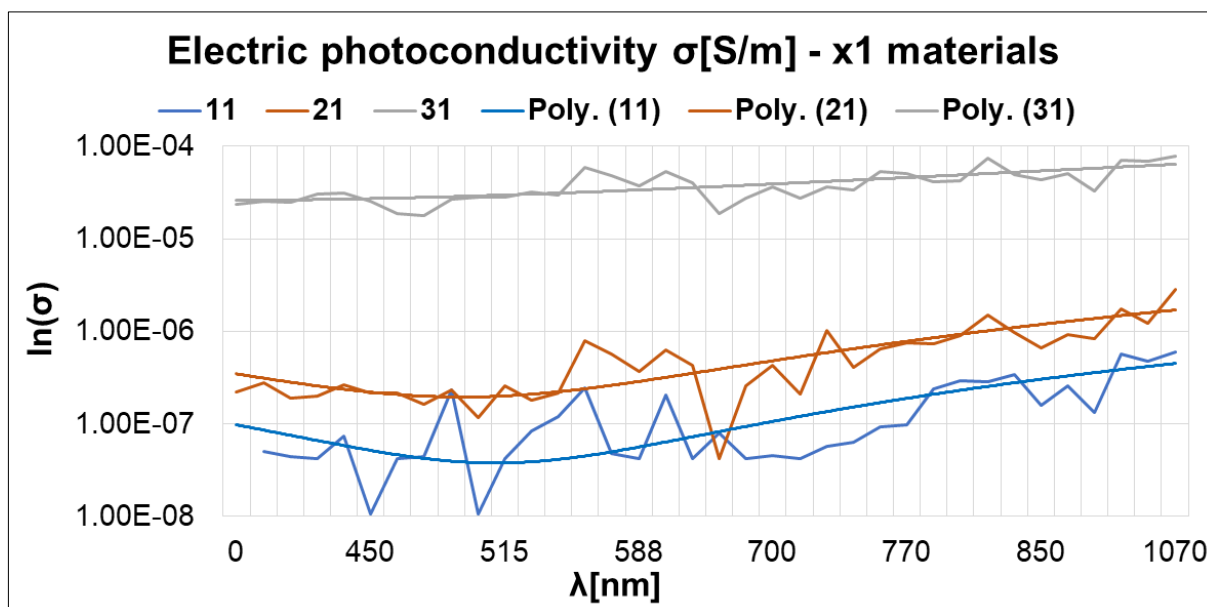
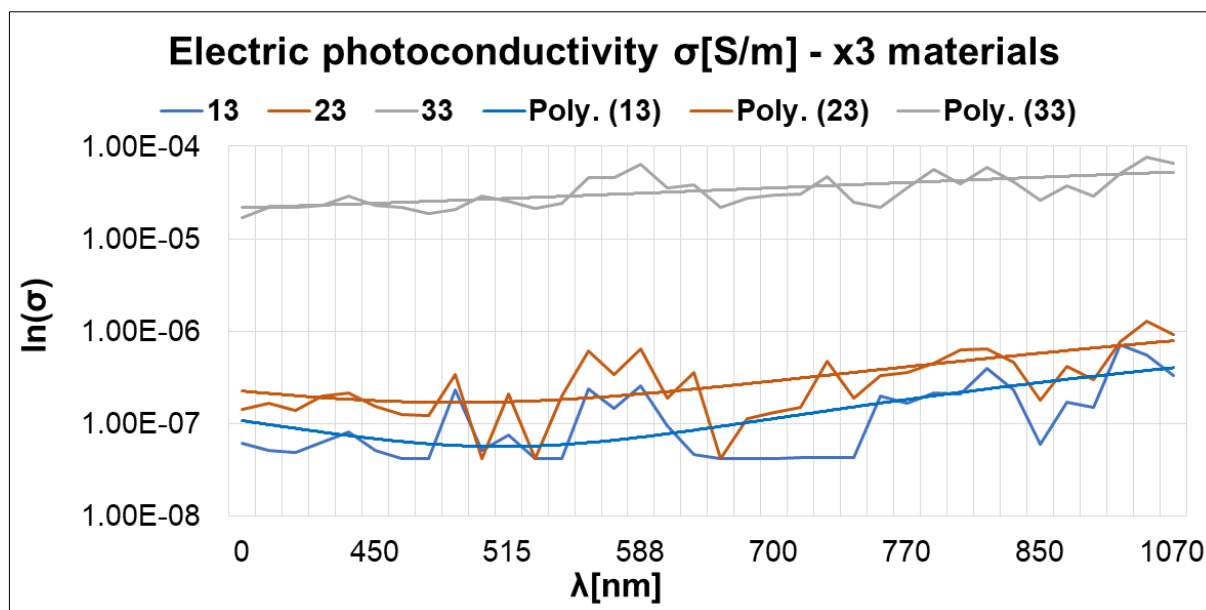**Figure 3.** Electric photoconductivity of materials formed on the first stage (without SEFs)
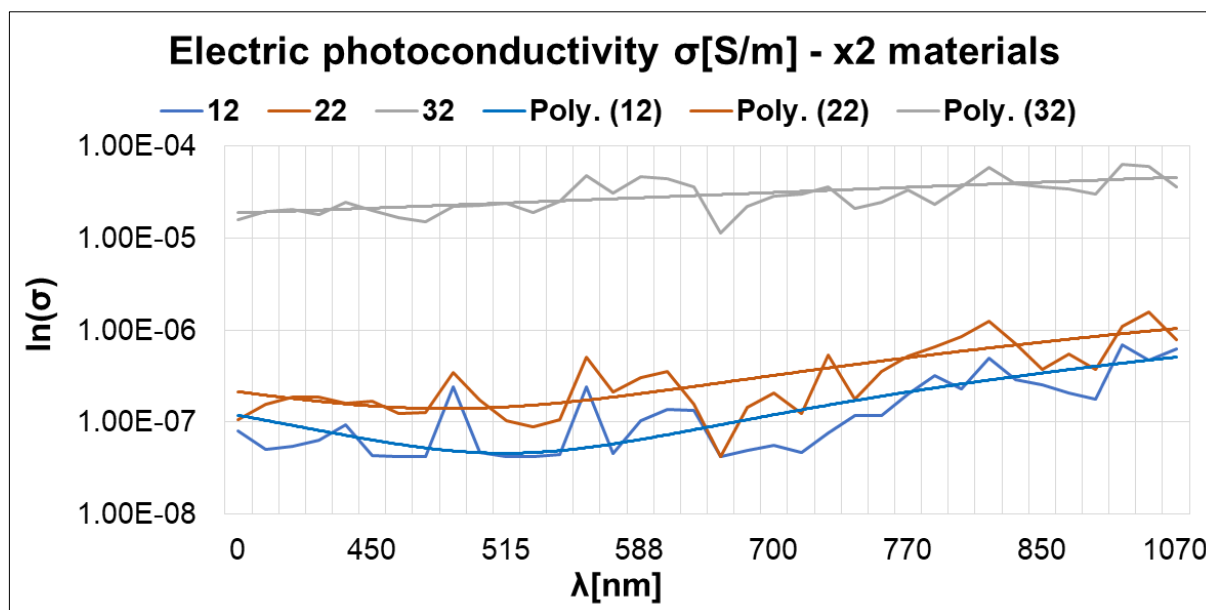
Figure 4. Electric photoconductivity of materials formed on the second stage (SEF1+SEF2)

A very short analysis of the presented data reveals that the electric photoconductivity of modified epoxy resin is 3 to 7 orders of magnitude higher than electric photoconductivity of epoxy resin. Another aspect that has to be pointed out is the general form of the recorded data - the broken line. This is due to the fact that we did not use a source of light with continuous variation of the wavelength but the above mentioned LEDs batteries generating 34 discrete values of the wavelength of the electromagnetic radiation. That is why this study is more qualitative than quantitative but offers information about the effect of the solution of metallic chlorides in DMF into the epoxy resin volume from the electric point of view.

Regarding the unavoidable measurement errors we have to precise that the most important source of such errors is the placement of the measuring electrodes on the sample meaning that is difficult to place the electrodes at the above mentioned distances. Other source of errors is given by the materials mechanical properties. When the material is soft probably the measuring electrodes are penetrating the surface of the material and perhaps the apparent diameter of the sample is changed.

The represented broken line are results of an average over three measurements, on the same sample, but in three different points and their aspect confirms the homogeneity of materials. We choose to represent also a fitted (second degree polynomial) curve to facilitate the results interpretation.

Analysing the data in Figure 3 to Figure 5, on one hand, it is obvious that the materials modified with 75mL of metallic chlorides in epoxy resin are showing the highest values of the electric photo-conductivity while the other two class of materials show electric photoconductivity values higher that the value corresponding to epoxy resin, but lower than the one corresponding to the x3 materials. On the other hand the difference between x1 and x2 electric conductivity seems to be constant with lower values for x1 materials. That is explainable by the different concentration of metallic chlorides in formed materials, but the values are enough close and both are distanced from the values corresponding to x3 materials. In such conditions it is difficult to conclude that there exists a direct proportionality between the metallic chlorides concentrations and the values of electric photoconductivity.

Figure 5. Electric photoconductivity of materials formed on the last stage (with all the SEFs)

Remembering that x is representing the period of solution preparation with applied sinusoidal electric field, the above observations lead to the conclusion that the preparation duration and the applied electric treatment are not affecting the electric photoconductivity of formed materials. This conclusion might be better understood analysing the representation of averaged values of electric photoconductivity in Figure 6.
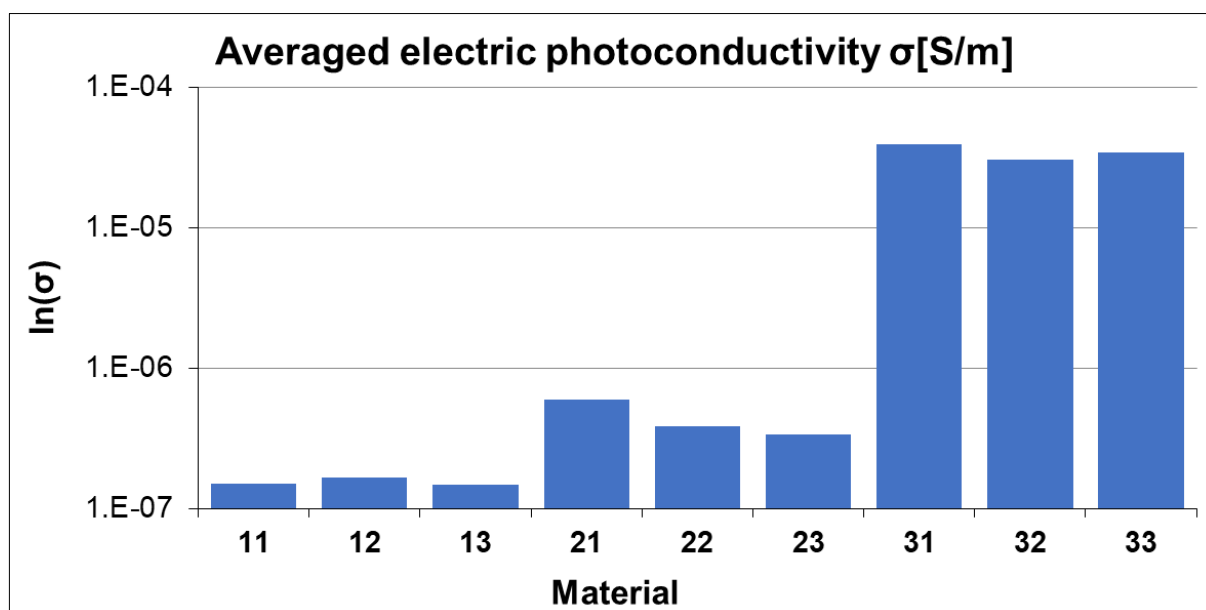
Figure 6. Averaged electric photoconductivity of analysed materials (based on formation moment)

It is easy to notice that the averaged values of electric photoconductivity are increasing when the amount of modifying solution increases, but from 1x materials to 2x materials the increase in value is lower than the one recorded for 3x materials. Also, it might be noticed the fact that there are some small differences between the averaged values of electric photoconductivity within each class of materials (depending on the formation moment and applied special treatments), but it is difficult to precise if they are consequences of forming or measurement errors. Apparently, there is no connection between the preparation process (including special electric treatment) and the electric photoconductivity.

Regarding the mechanical properties of the formed materials, as we already presented above, we tested all the materials on tensile and three point bending fixtures. For each type of test we used five samples and we present the averaged curves for each of the nine materials in Figures 7 - 9. We decided to present only the data for very small specific deformations - to be able to emphasise the small differences between materials formed on the same stage but with the three different volume ratios (vr) of metallic salts solution in DMF.
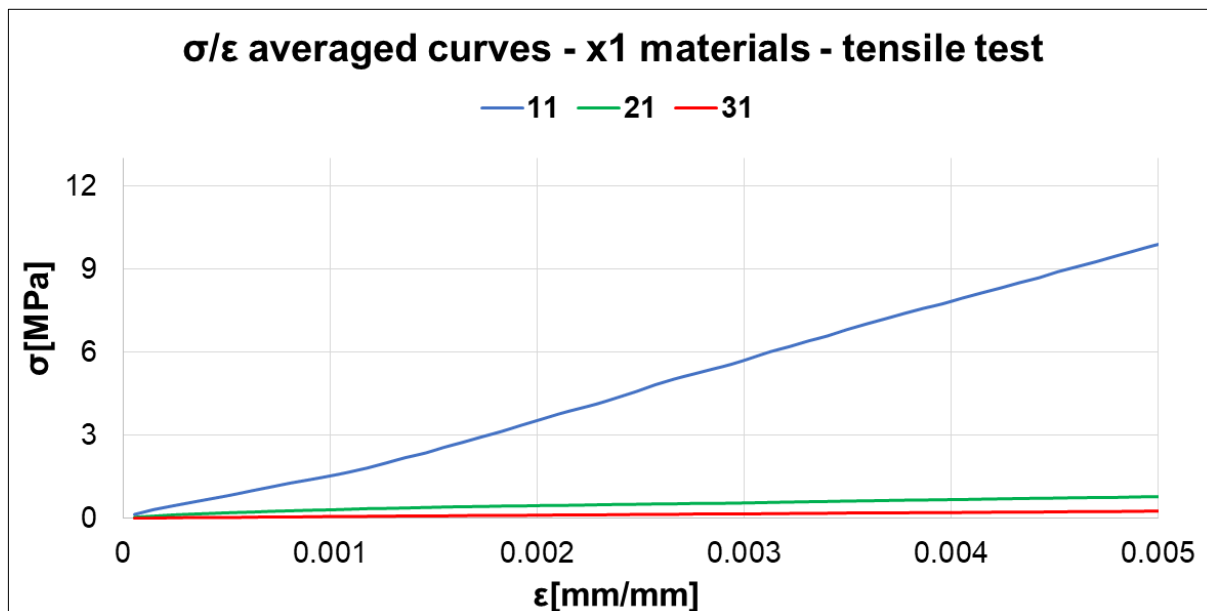

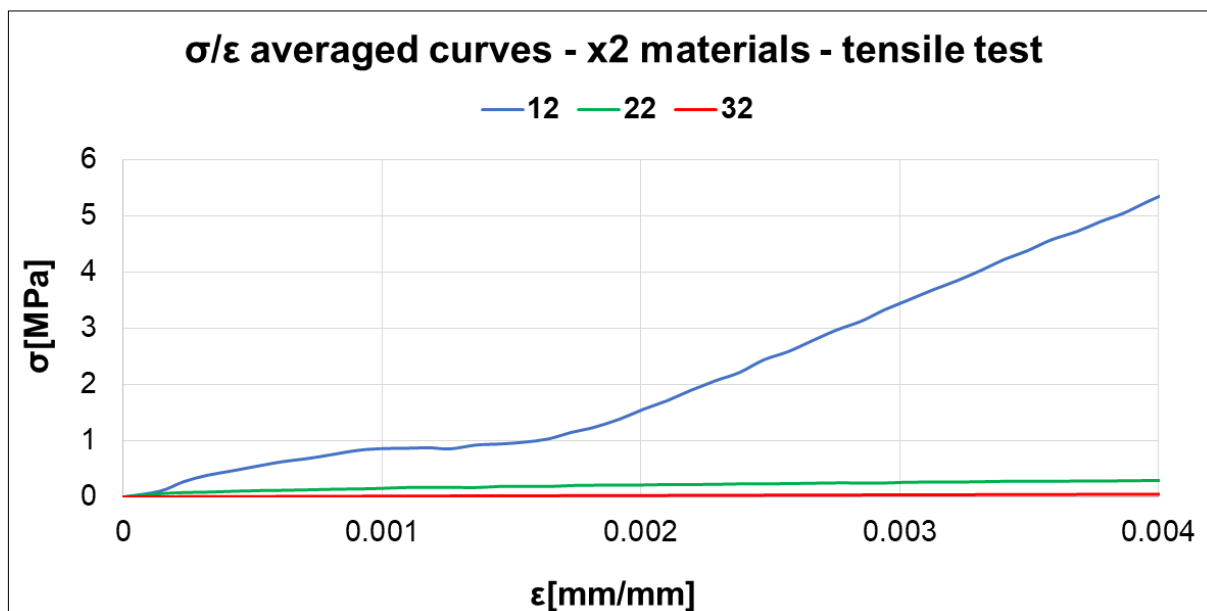**Figure 7.** Averaged tensile behaviour of x1 materials – tensile test

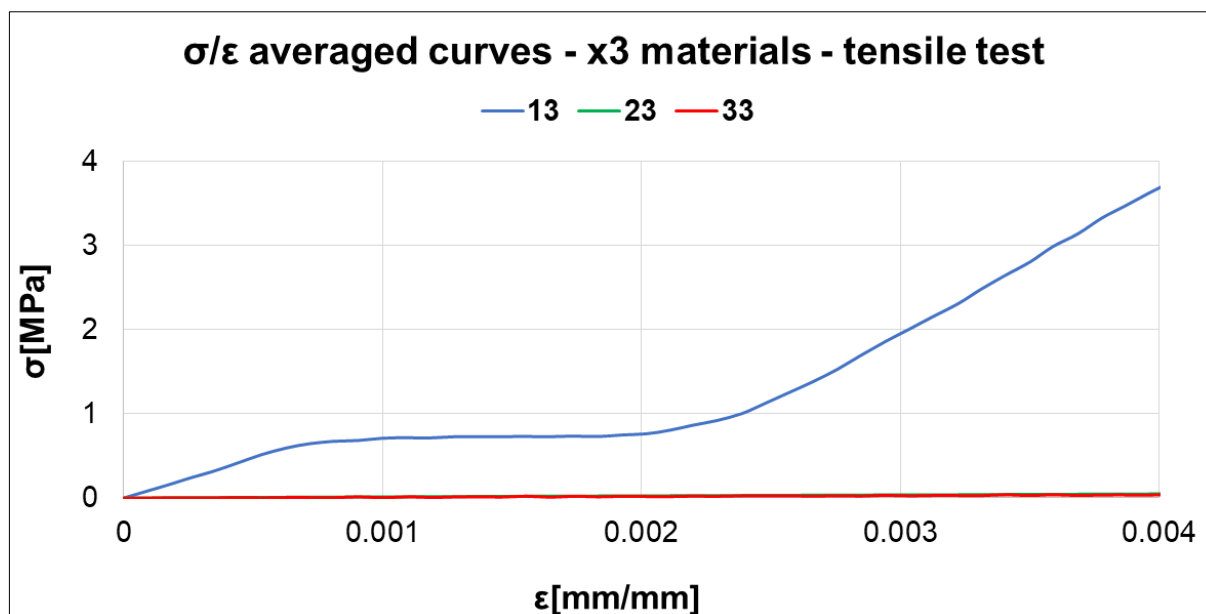**Figure 8.** Averaged tensile behaviour of x2 materials – tensile test

Figure 9. Averaged tensile behaviour of x3 materials – tensile test

This study is part of a larger one in which we determined the tensile elastic modulus for the epoxy resin as being of 2.5GPa, and bending elastic modulus as being of 2.8GPa. Analysing the data in Figure 10 it is obvious that adding the three amount of metallic chlorides solution in DMF the values of the tensile elastic modulus are decreasing, but unlike the case of electric photoconductivity, in this case there is a decrease due to the period of preparation prior to forming moment (and, of course, due to the electric treatments). As long the preparation period is as higher is the decrease in tensile elastic modulus value.
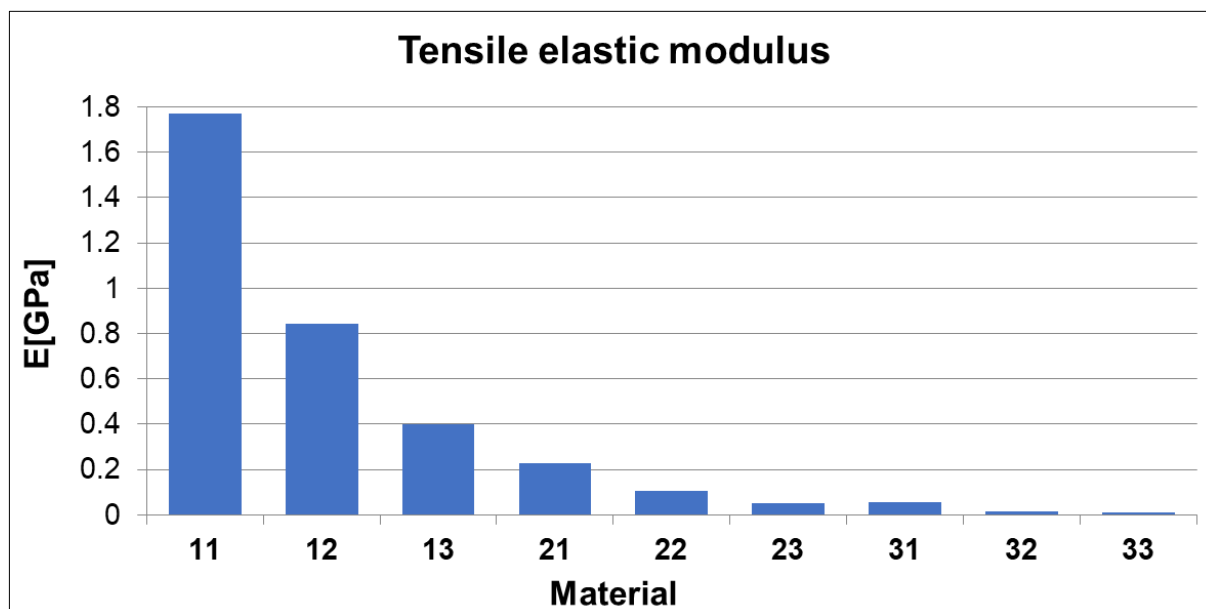

Figure 10. Tensile elastic modulus of analysed materials (based on formation moment)

Regarding the results of three point bending (Figures 11-13) again the decision was to represent the acquired data just for small displacements because in the case of materials with 0.15 and, respectively, 0.20 vr of DMF solution we recorded very large displacements, up to 30mm (after the test all the samples recovered their initial form). As in the case of tensile tests the values of bending elastic modulus are depending on the volume ratio of DMF solution of metallic chlorides in the final material and the effect resides in the decreasing of bending modulus values (relative to the value of the bending modulus of

epoxy resin). In the case of bending tests the dependence of bending elastic modulus on the duration of the preparation period is not as clear as in the case of tensile tests, at least for 1x materials, but again we could talk about experimental errors - in this case misalignment of the sample on the experimental fixture or small variations of the samples thickness. As per bending elastic modulus (Figure 14) its values are dramatically reduced (with respect to the bending elastic modulus of epoxy resin) due the presence of the solution. For the lowest value of solution's vr in the epoxy resin the decrease is of three orders of magnitude. For the other two values of solution's vr in the epoxy resin it is impossible to consider that the materials are showing an elastic behaviour in bending.
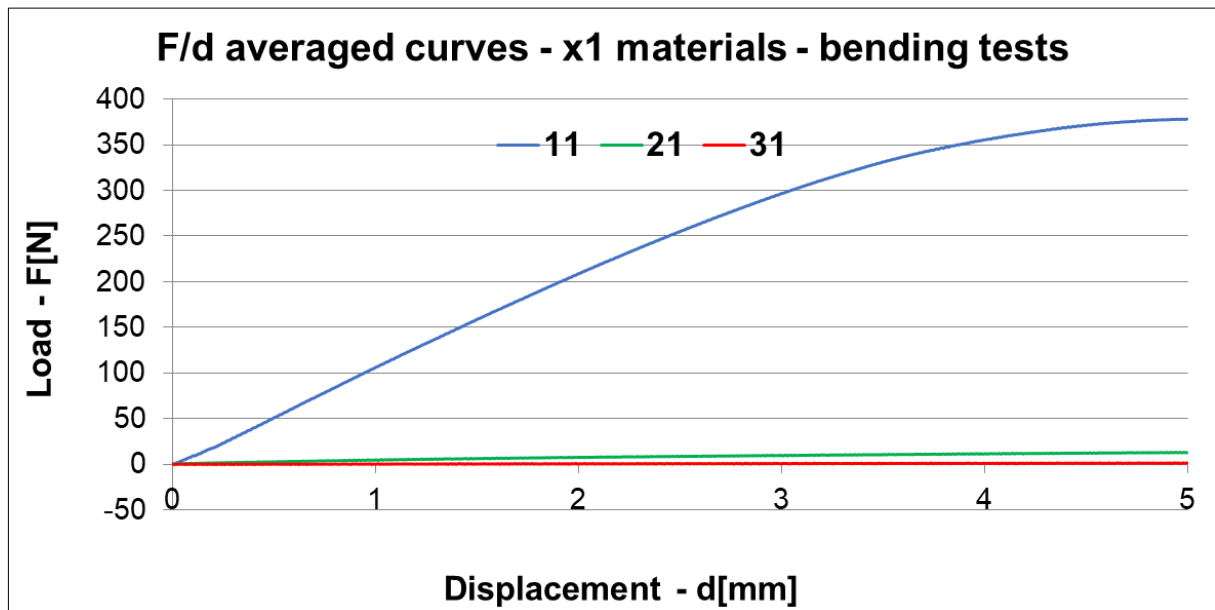
Figure 11. Averaged bending behaviour of x1 materials – three point bending test
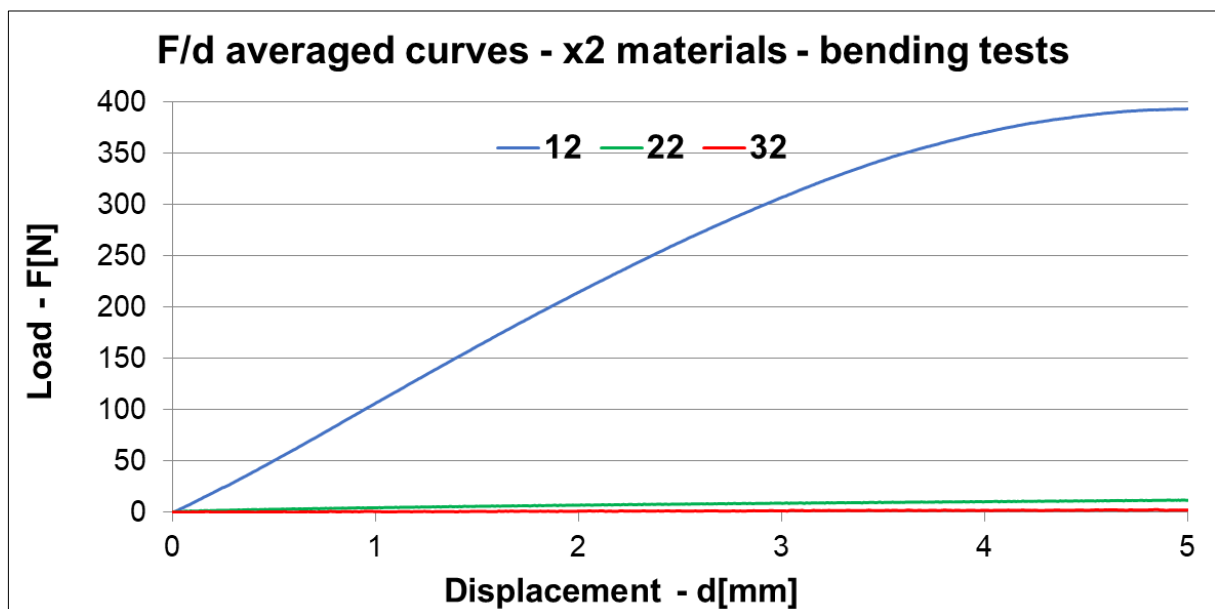
Figure 12. Averaged bending behaviour of x2 materials – three point bending test
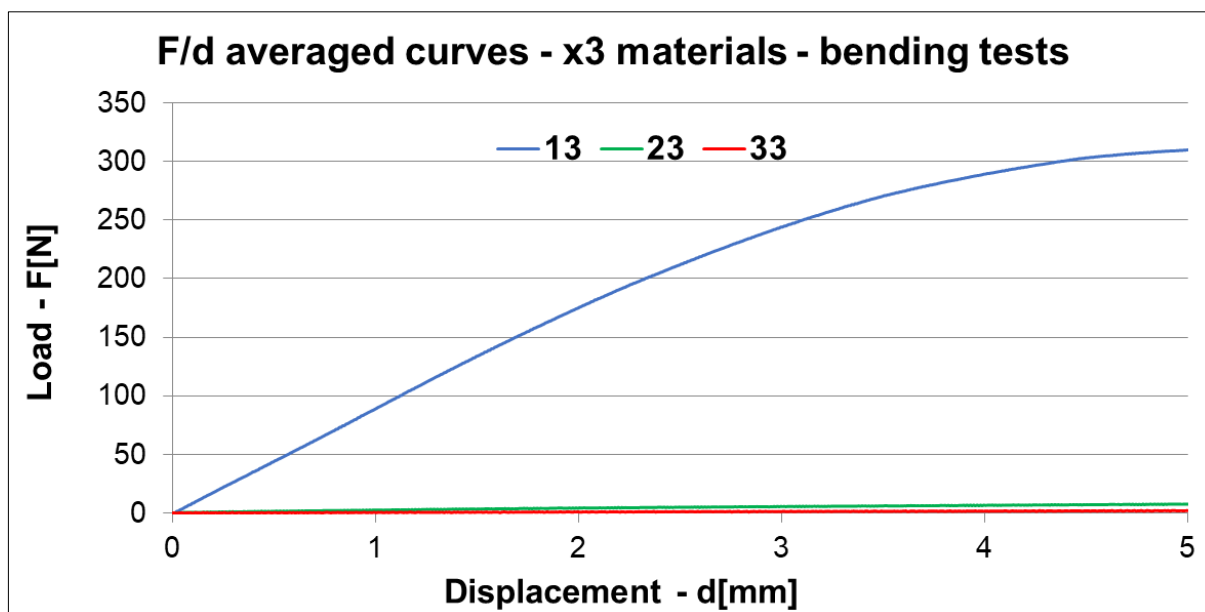
Figure 13. Averaged bending behaviour of x3 materials – three point bending test
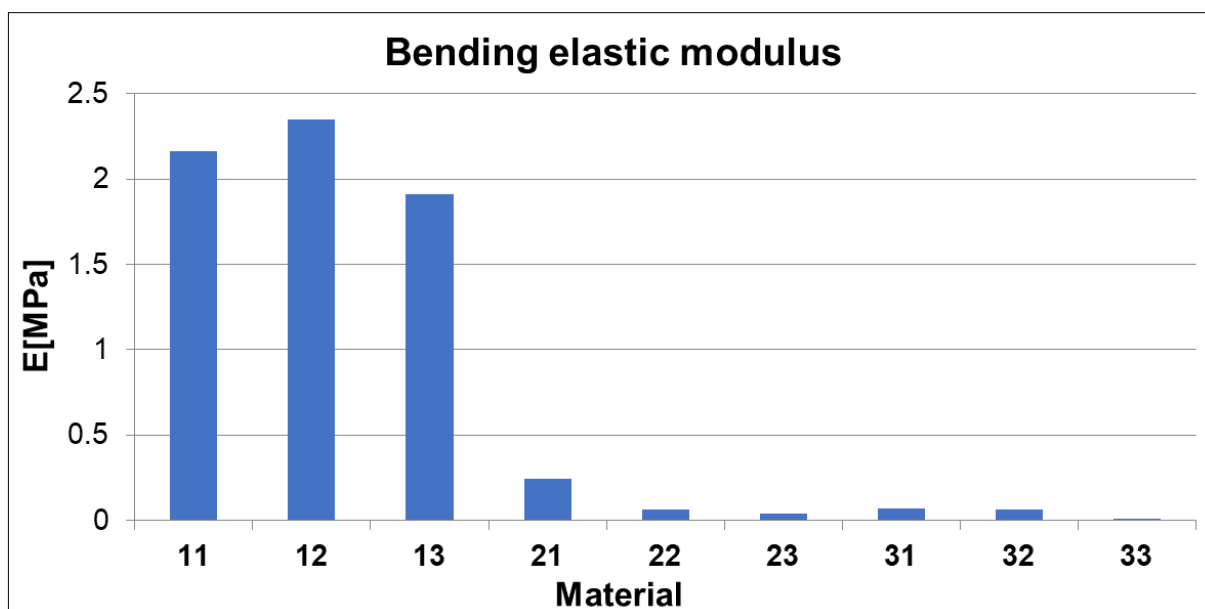

Figure 14. Averaged bending elastic modulus of analysed materials (based on formation moment)

4. Conclusions

The starting point of this research was the hypothesis of changing the electric conductivity of a polymer by placing into its volume some metallic ions (especially d type metals, such as Yttrium and Copper). Having many free energetic levels, these metals' ions could determine semiconductor type conduction (electrons and holes) of the material. Because it is difficult to bond independent atoms (or ions) we try to use solutions of inorganic salts to reach the above mentioned goal. More, it is known the existence of very special complex oxide YBCO (Yttrium, Barium, Copper, oxide) – $YBa_2Cu_3O_x$ with special properties. That is why we decided to use chlorides of Yttrium, Barium and Copper dissolved in DMF trying to investigate also the formation of nano-YBCO due to the energy resulted from the reaction of polymerisation. Therefore, the dissolved amounts of Yttrium chloride, Barium chloride, and Copper chloride were determined according to YBCO stoichiometry.

Certain amounts of solution (that has been stabilized after 50 days) were homogenized together with the main component of the epoxy resin (RE4020) and the necessary amount of hardener was added

(DE4020) such as, at the end, the volume ratio (vr) of salts solution into the epoxy resin to reach values of 0.10, 0.15, and 0.20, respectively.

Assuming also that the solution contains ions (metallic ions, chlorine ions) we applied for various durations a sinusoidal electric field (through graphite electrodes) hopping, on one hand that the electric field will unbalance the ionic equilibrium leading to new chemical bonds and, on the other hand, hopping to eliminate chlorine from the solution. Therefore we formed and analysed nine materials. The analysis pointed electric photoconductivity and mechanical properties of formed materials (tensile tests and three point bending tests).

The electric tests showed higher values of electric photoconductivity of the modified materials with respect to the electric photoconductivity value of epoxy resin – 3-4 orders of magnitude in the case of the materials modified with 0.10, and 0.15 vr of metallic chlorides solution in DMF, and 6-7 orders of magnitude in the case of 0.20 vr of metallic salts solution in DMF modified materials. The increase of electric photoconductivity values (with respect to the volume ratio of the modifying solution) is not linear so it cannot be concluded that the electric photoconductivity value is proportional with the metallic ions concentrations in the final materials.

There are some variations of the averaged values of electric photoconductivity of materials but it is difficult to decide if they are effects of different periods of preparation of the solution prior the materials formation. It is also the case of applied sinusoidal electric field - we cannot conclude if it contributes to the variations of averaged electric photoconductivity values for analysed materials.

In the case of the tensile tests, the determined values of tensile elastic modulus are showing without any doubt that both the volume ratio of the modifying solution and the duration of preparation contribute at the decreases of tensile elastic modulus values with respect to the value of tensile elastic modulus of epoxy resin. Once the volume ratio of solution in the final material increases the material becomes softer. We may associate the softness of the material with a less compact polymer network (due to the presence of DMF). A softer material allows much easier the movement of the electric charged particles contributing to the increase in electric photoconductivity value.

The three point bending tests results confirm the inverse proportionality between the modifying solution vr and the value of the bending elastic modulus, but it is not possible to decide the same about the duration of solution preparation prior the formation of materials.

However the presented mechanical properties are far away from the mechanical properties of the epoxy resin and these materials (eventually excepting 1x) cannot replace the epoxy resin to form, for instance, fibre reinforced composites or fabric reinforced composites. Being very soft the 0.20 vr metallic chlorides solution in DMF might be used as thin films covering traditional epoxy resin composites ensuring a higher conductivity of the external layers.

The volume ratio of the solution is the same but the metallic ions concentration is not because during the preparation periods some amounts of DMF (or/and chlorine) vaporize leading to a higher concentration of the inorganic agents. In this respect some materials could be formed after a long preparation (high inorganic agents' concentration) due to the DMF vaporization. The required amount of DMF used in this study was calculated such as to ensure dissolution of required quantities of inorganic agents. During the long period of preparation and forming of all materials we did not notice precipitates in the solution pot so the solution was stable. In such conditions it is possible to realise the study with higher concentrations of inorganic agents and smaller amounts of DMF.

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