Journal of Materials and Electronic Devices 4 (2022) 34-39

FYTRONIX
JOURNAL OF
MATERIALS AND ELECTRONIC DEVICES
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The Effect of Various Sol-Gel Doping on Epoxy Resin

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We have studied the mechanical and electrical properties of several sol-gel mixtures with the epoxy resin (Duratek DTE 1200) for the first time. The spectrum of the samples ranges from 5% and 10% to 15% of the volume of sol-gel to the host resin. These sol-gel samples are pure BaZrO2, Mn, and Zn doped BaTiO2 and La-Sr half-half doped YZr2O7. These samples were prepared by the sol-gel technique and added to the epoxy resin with the volumes mentioned, including the hardener. The effects caused by the addition of the sol-gel samples into the epoxy resin were investigated with a micro-hardness tester. The effects on the electrical properties of the samples were studied using the room temperature dielectric measurements. Polarized light microscopy technique was used to define the change in the microstructures of the epoxy with these dopants. We have observed an increase in the hardness of the epoxy resin with an increase in the quantity of sol-gel mixtures for BaZrO2, Mn and Zn-doped BaTiO2 while a decrease was observed for La-Sr half-half doped YZr2O7. The dielectric spectrum measurements over these samples showed a correlation with structural changes. The samples which got harder showed a dynamical dielectric behavior with some relaxation spectrum while the other sample which got softer became more conductive and did not show any relaxation signature.

Keywords: *Sol-gel technique, Epoxy resin, Doping, Mechanical and electrical properties*

Submission Date: 04 November 2022
Acceptance Date: 08 December 2022

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1. Introduction

The production of composite epoxy resin with sol-gel solutions is more advantageous than the conventional solid-state techniques even for production involving nanoparticles. This is mostly due to the higher possibility of producing homogeneous solutions with the sol-gel method. Here, the sol-gel process involves hydrolysis and condensation reactions with hydrolysable metal alkoxides known as alkoxysilanes. When using organo-alkoxysilane as the coupling agent in sol-gel solutions, stronger atomic bonds can be created between organic and inorganic phases isotropically which is crucial for increasing and improving the mechanical and electrical properties of the produced sample [1]. The main idea for the use of composite materials is to take advantage of the best properties of the polymeric materials including inorganic structures while at the same time reducing the disadvantages of the polymers [2]. These disadvantages are mostly related to the mechanical properties of the polymers such as weakness, softness, etc. Thus, the combination of sol-gel solutions with resin possesses more industrial application potential by overcoming these known disadvantages. With this method, various types of monomers and polymers can be conveniently used in the production of organic-inorganic composite materials. The ratios of the inorganic to organic compounds in the composite material production can easily be controlled by varying the relative volumes of the starting compositions. This full control yields the ability to change the chemical properties of the material which also changes the application spectrum of the end product.

The combination of hardness and thermal stability of inorganic glass and toughness of organic matrix leads to composite materials with improved thermal and mechanical properties [3, 4]. Out of a list of applications, sol-gel composite materials have been used as protection against corrosion, which is a major environmental problem. In relation, sol-gel derived materials are also used as protection against decay caused by unwanted chemical reactions and the loss of material due to corrosion [5]. Composite coatings have been found to provide excellent corrosion resistance and an insulation for metal substrates based on their ability to form significant barriers against penetration of corrosion inhibitors [6, 7]. Due to their versatility, we can say that sol-gel composite epoxy materials are very fertile materials for creating new usage areas, including coating applications. However, we still need an in-depth understanding of all chemical reactions and incidents occurring not only in the sol-gel but also in the epoxy curing processes in order to produce materials with the desired properties. The mechanical properties of the composite materials can be controlled mostly by the inorganic content in the process which usually introduces hardness and sometimes brittle behavior [8–10]. Here, a good example is DGEBA/Jeffamine D-400 composite materials where the mechanical characterizations are improved by adding TEOS in different volume ratios as an SiO2 source [11].

In this study, we examine the change of the mechanical characteristics of the epoxy resin by measuring hardness and electrical properties under the doping of BaZrO2, Mn and Zn doped BaTiO3 and La-Sr half-half doped YZr2O7 sol-gel solutions. These inorganic sol-gel solutions are added to the resin in 5%, 10% and 15% volume ratios where the host resin (DURATEK DTE 1200) consists of 72% epoxy and 28% hardener.

2. Experimental Procedure

The sol-gel solutions used in this experiment were prepared according to a procedure detailed as follows. BaZrO2 solutions were prepared using barium (2,4) pentanedionate and zirconium (2,4) pentanedionate powders . The solutions of Mn-doped BaTiO3 were prepared by mixing titanium isopropoxide, manganese (II) chloride tetrahydrate and barium (2,4) pentanedionate . Half-half Sr/La doped (Sr0.5La0.5) Y2Zr2O7 solutions were prepared by mixing lanthanum nitrate hexahydrate, strontium isopropoxide and zirconium (2,4) pentanedionate with yttrium nitrate hexahydrate. For the last sample, which was Zn doped BaTiO3, the solution was created by mixing zinc chloride, barium (2,4) pentanedionate and titanium isopropoxide. These mixtures were dissolved in mixture composed of glacial acetic acid, ethanol, and methanol. In order to ensure the homogeneity of the total solution, 5 ml of triethanolamine was added and the pH of the whole mixture was checked and controlled during these steps. The solution was stirred for 24 hours at room temperature. Clarity and the homogeneity were checked visually every two hours.

At the end of this mixing procedure, all the sample solutions were found to have a pH value in the range of 5 and 5.5. These solutions were added to the epoxy resin solution containing 72% by weight epoxy and 28% by weight hardener. For the experiments, 5%, 10%, and 15% by volume of each sol-gel sample were mixed creating a doped solution for the epoxy resin. The final sol-gel solution including the epoxy was again stirred with a mechanical stirrer and allowed to harden for another 24 hours. At this stage, a sol-gel/epoxy composite material was created. For the final stage of the sample preparation, these composite materials were cured at 80 °C for one hour in the air. The physical appearances of the samples at this stage are shown in Fig. 1 for a couple of doping compounds with the pure epoxy as well. Following completion of the curing process, the mechanical properties of each sample was measured using a hardness tester (Buehler Hardness Tester 2000) and their surfaces were examined by polarized light microscopy (LEICA DM 2500 Optic Microscope). In order to get an accurate value, five different parts of each sample were measured, and the average of the hardness values was used. For the electronic characterization, we used an Agilent LCR network analyzer to determine the dielectric properties of the samples. The dielectric measurements were conducted at room temperature without any field.

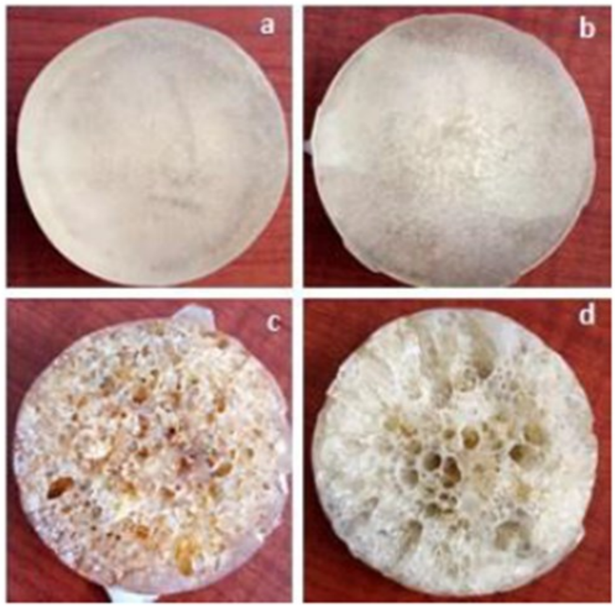

Fig.1. The cured samples of (a) epoxy resin, (b) cured BaZrO2 sol-gel mixture in epoxy resin, (c) Mn-doped BaTiO3 composite material, and (d) half-half doped Sr0.5La0.5YZr2O7 composite material.

3. Results and Discussions

The first step of mechanical characterization was done visually using polarized light microscopy technique. Example of the pictures obtained from the sample surfaces for the 10%-doped composite materials are shown in Fig. 2. Each picture was magnified 10 times and as can be seen from this figure, microstructures were formed resembling pores and clusters lying on the surface of each sample. The size of these clusters is small for La0.5Sr0.5 YZr2O7 compared to the ones found in BaZrO2- and Mn-doped BaTiO3 epoxy samples. The addition of the dopant used in this study into the epoxy resin material considerably effected the curing time needed to isotropically solidify the epoxy. This curing time was observed to be shortened up to 6 times with respect to the pure epoxy material's curing time. During the curing process, the doped samples produced some exothermic reactions which also increased the temperature of the solution. The shortening of the curing process was found to be inversely proportional to the doping amounts in the epoxy resin.

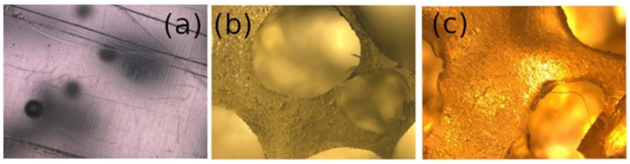

Fig.2. Microstructure images of the doped epoxy / sol-gel composite materials with a magnification of 10x. (a) Sr0.5La0.5YZr2O7-, (b) BaZrO2-, and (c) MnBaTiO3-doped epoxy / sol-gel cured sample.

The results of hardness measurements are shown in Table 1 for all the doped samples, in addition to the pure epoxy resin sample, for which the hardness was measured as 9.13 HV (taken as the reference for other measurements). The doping effects created by BaZrO3, Mn-doped BaTiO3 and Zn-doped BaTiO3 was found to elevate the hardness of the mixtures. The effect of the change in the hardness is observed to be in the range of 20% to 25% for 5% to 10% doping for all the samples, while there is an enormous increase in the hardness, in the amount of 400%, for the 15% doped BaZrO2 sample. As seen from Table 1, the general behavior of the increased additive in the epoxy results in an increase of composite mixture hardness except for the Sr0.5La0.5YZr2O7 sample. Unlike the other three doped samples, the addition of Sr0.5La0.5 to YZr2O7 showed a decrease in the hardness. This decrease is considerably less up to 10% addition; however, for 15% doping, the observed hardness decreases by as much as 50% with respect to the pure epoxy values.

Table 1. Results of the hardness measurements. The percent values are the doping ratios.

Sample	Average Hardness [HV]
Epoxy Resin (pure)	9.13
5% BaZrO2	9.63
10% BaZrO2	11.7
15% BaZrO2	32.6
5% Mn-doped BaTiO3	5.55
10% Mn-doped BaTiO3	10.53
15% Mn-doped BaTiO3	12.03
5% Zn-doped BaTiO3	11.7
10% Zn-doped BaTiO3	11.85
5% Sr0.5La0.5YZr2O7	9.2
10% Sr0.5La0.5YZr2O7	8.76
15% Sr0.5La0.5YZr2O7	4.96

To improve the micro-structural characterization, we also performed frequency-dependent dielectric permittivity measurements on our samples. The results of these measurements were gathered in two main groups depending on their frequency-dependent dielectric behaviors, shown in Fig. 3 and Fig 4. Each figure has the pure epoxy resin dielectric response shown in black, in order to be used for comparison with the doped composite results. One main common behavior of all the samples was the increase in real and imaginary parts of the dielectric permittivity with respect to the pure epoxy resin. This is evidence for the existence of trapped charges in the epoxy polymeric matrix created by the ceramic dopants. This behavior is also supported by the increase shown in the tan-loss data in panel

(b) in each figure. The dynamically active samples are shown in Fig. 3. These are BaZrO2, Mn-doped and Zn-doped BaTiO3 epoxy composite samples presented in blue, green, and red, respectively. All the data shown are for 15% doped samples except for the Zn-doped sample. For the Zn-doped BaTiO3, the measurements were conducted on the 10% doped mixture. The dynamically active samples shown in Fig. 3 have some weak relaxation-like features which are especially dominant for the Mn-doped BaTiO epoxy mixture. This weak absorption manifested as a hump at the frequencies centered at 104 Hz in ε'' data. This is also supported by the tan(δ) data shown in the inset of panel (b) in Fig.3. The decrease in ε' data for this sample over the 104 Hz frequency can also be seen in panel (a) of this figure. We can estimate a better polarization of the charges at this region of frequencies for Mn-doped BaTiO3 epoxy composite sample [14]. The BaZrO2-doped epoxy sample shown by blue color has an increasing dielectric response in both real and imaginary parts of the dielectric constant. This is also valid for the conductivity and dissipation loss factor data as well. The conductivity and dissipation loss factor are depicted in the insets of each panel in Fig.3 and 4. On the other hand, the Zn doped BaTiO3 epoxy sample, shown in red, has even less changes than the rest of the samples; however, it still contains some very weak relaxations and a very low increase in all dielectric responses.

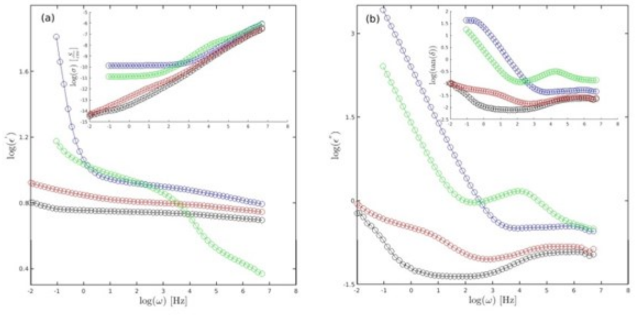

Fig. 3. Dielectric susceptibility, conductivity, and dissipation loss factor of the samples as a function of frequency. **(a)** Real part of the dielectric susceptibility along with the measured conductivity (inlet). **(b)** Imaginary part of the dielectric susceptibility along with the dissipation loss factor (inlet). Color coding: pure epoxy resin (black); BaZrO2 (blue); Mn-doped BaTiO3 (green); Zn-doped BaTiO3 (red).

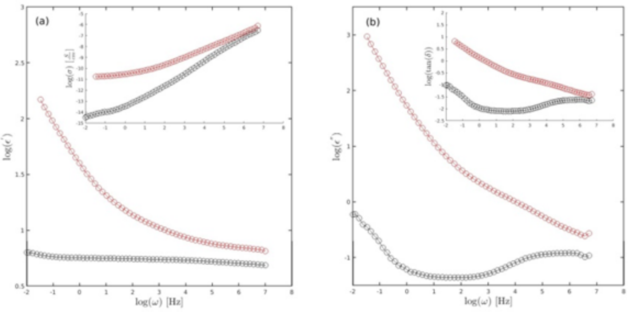

Fig. 4. Dielectric permittivity, conductivity, and dissipation loss factor of the samples as a function of frequency. **(a)** Real part of the dielectric of the dielectric permittivity along with the measured conductivity (inlet). **(b)** Imaginary part of the dielectric permittivity along with the dissipation loss factor (inlet). Color coding: pure epoxy resin (black); La0.5Sr0.5YZr2O7 (red).

The different behaviors regarding the characteristics seen in the Mn-doped BaTiO3 epoxy resin material can be attributed to the additional magnetism originated from Mn ions which contribute to the electric conductivity in this sample [15]. The same conclusion can also be consolidated with the dielectric behavior of Zn-doped BaTiO3 epoxy sample. This response of sample is the weakest one following closely with the values of the pure epoxy resin data. This can be explained by the dilution effect of Zn ions in the ceramic doping of BaTiO3.

In the latter figure, the results for the composite sample of La0.5Sr0.5YZr2O7 are given. Unlike the behavior shown in Fig.3, La-Sr half-half doped YZr2O7 epoxy resin composite material, shown in Fig.4 has greatly increased dielectric values of ε' and ε'' in panels (a) and (b) as the frequency decreases. The increase is monotonical and more noticeable than the rest of the samples without any sign of relaxation. This can be attributed to the elevated conductive behavior of the La0.5Sr0.5YZr2O7 epoxy resin composite system.

4. Conclusion

The main outcome of this study was the shortening of the curing time of the epoxy resin (72% epoxy with 28% hardener) DGEBA/Jeffamine D-400. It was observed that the time needed to completely dry the epoxy resin was decreased by almost six times. The ceramic-based samples mixed in the host epoxy resin quickly hardened to form a composite material. The resulting hard composite structure had a higher hardness value for BaZrO2, Mn, and La-doped BaTiO3 while the opposite behavior was observed for La-Sr doped YZrO7. La-Sr doped YZrO7 epoxy composite showed less hardness with respect to the pure epoxy resin. Interestingly the dielectric permittivity measurements conducted between 10−2 to ∼106 Hz show a dynamical behavior including weak relaxation-like signals at the medium range of the frequency at room temperature. This was observed for BaZrO2, Mn, and La-doped BaTiO3 doping. The Mn-doped BaTiO3 epoxy composite sample showed this relaxation dominantly in the ~104 to ~105 Hz region signaling for unusual dipole interactions. These dielectrically active samples were the ones which demonstrated the most hardness when the epoxy was cured. Several other explanations for the unusual characteristics seen in these samples should also be considered. For example, possible lattice distortions in the ceramic doping, the heterovalent substitution in the metallic doping of Mn and/or La in the ceramic BaTiO3 samples can be counted here. In addition, possible doping vacancies with or without oxygen vacancies as well in the ceramic dopants can also be the reason for the cause of these observations [12, 13]. These effects cultivated with the amorphous structure of the epoxy resin would end by a complex motion and distribution of ions observed especially for imaginary part of the dielectric permittivity shown in Fig.4. At this moment, we do not have any conclusive explanation for not having the same active behavior for the La-Sr-doped YZrO7 epoxy sample. Further examinations like x-ray scattering analyses are needed to solve and to understand the insight of these mysterious electrical behavior; however, the amorphous structure of the epoxy as the host material for this composite sample makes it difficult if not impossible to do so. We would like to emphasize that the samples which showed more hardness and quick curing characteristics are valuable for commercial applications and usage. Thus, we believe this preliminary research into the subject of sol-gel composite material preparation by ceramic doping into epoxy resins will have an impact on future applications of resin manufacturing and development.

Acknowledgement

This research was supported by Akdeniz University's research initiative (BAP 4242).

Declarations

The research methods mentioned in this article do not pose any ethical issues. The authors have no conflicts of and/or competing interests to declare.

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