Surface and Interface Investigations of Matrix–Fillers in Heterogeneous Amorphous Semiconductors

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ABSTRACT: Phosphate glass-based composites are prone to be as effective as amorphous semiconductors, enhancing the glass properties by the addition of a small amount of metallic fillers (Cr, Co, Ni, and Zn) and leading to the creation of composite materials where the conductive particles can be distributed in the glass matrix PbO–P₂O₅ (PbP) at the micrometer level. This paper deals with scanning electron microscopy (SEM) examination and the wetting behavior of the phosphate glass–metal powder composites. We focused on the filler effect on wetting characteristics, such as interfacial free energy. The change in the contact angle of water on the glass surface was also measured. Scanning electron microscopy images of the composites showed a good dispersion in the fillers within the glass matrix. The contact angles of the composites with water and three polar and apolar solvents were calculated. The total solid surface free energy was analyzed. The interaction parameter between the composites and the liquid has been calculated using Owens–Wendt equation.

I. INTRODUCTION

Recently, phosphate glass-based composites have attracted much attention as a simple and cost-effective material to enhance glass properties by conductive particle loading.¹−⁵ According to several studies, the interface exchange between matrix and filler plays an important role in the physical properties of materials (stability, mechanical, electrical properties, etc.). Thus, the aim of this work is to visualize the interface of the elaborated composites (PbP/metals) using scanning electron microscopy along with energy-dispersive X-ray (EDX) analysis. Also, we attempt to estimate the surfaces and the matrix–filler interface energies of composites through contact angle measurements.

Another important parameter that is examined on this occasion is the wettability of the obtained composite materials. Indeed, in recent decades, the study of wettability has received great interest. From a fundamental point of view, it is important to understand the nature of the interactions that are established between the liquid and the wetted surface and why some liquids wet and spread on given solid surfaces and not on others. This wettability phenomenon plays an important role in many industrial applications, such as adhesion in all painting processes of automobiles, textiles, adhesives, printing, liquid coating, oil recovery, painting, lubrication, electrowetting, self-cleaning, nanofluidics, and more.⁶

Concerning our studies, it is important to know how our elaborated materials behave “in the presence of liquids: water or others”. This parameter is of crucial importance in possible applications, such as solar or thermoelectric devices.

Usually, wettability is deduced from the measurement of the contact angle of a liquid droplet on the surface of solid material. There are different methods to measure the contact angle. Indeed, the measurements of contact angle allow the determination of the solid surface tension and solid/liquid interface tension. Then, the wetting characteristics of solid material are highlighted.

I.I. Morphology Study of PbO–P₂O₅ (PbP)/Metal Composites. It is well recognized that the morphology of the investigated composites has a major impact on their physical properties. Therefore, to obtain morphological insights into the elaborated composites, scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) analyses were undertaken. Indeed, SEM micrographs with high magnification permit us to observe the characteristic evolution of particle distribution. However, it should be noted first that it is not obvious to obtain a homogeneous dispersion of the fillers within the matrix. Indeed, many problems can be encountered. This is the case with the agglomeration of the fillers, which prevents dispersion and decreases the viscosity of the matrix. This needs a lot of work, and it takes time to achieve a good result. Thus, the obtained results on PbP/metal composites at low and high

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loading inside the glass matrix are given in Figures 1–4, with the EDX spectrum, and mass and atomic percent. The above figures exhibit micrographs of sintered composite samples. It should be noted that the EDS analysis depends on...
where the probe is pointed. Therefore, the given percentages (weight, atomic) do not represent an overall analysis of the sample area. Features or phases as small as 1 μm or less can be analyzed.
Note that at a low inclusion rate, the particles are obviously farther apart, and then at elevated filler loading, the metallic particles are more and more in contact. We can see clusters of particles within the matrix. Also, continuous chains appeared inside the composite. At higher loading, the incorporated fillers form the so-called infinite cluster, which enables the conduction of the electrical current.

The energy-dispersive X-ray (EDX) analysis technique was employed to obtain additional information on the loading concentration through EDAX signals and to observe if there was any appearance of new phases or important impurities. Indeed, some minor intensity peaks related to impurities are detected. The detected carbon is likely generated from the carbon tap used to fix samples on the substrate while performing SEM analysis. Also, we note Al impurities in a very small quantity, which originates from the used alumina crucible during the glass synthesis.

Figure 5. SEM image, corresponding elemental maps, and energy-dispersive X-ray spectroscopy elemental mapping of PbP/Co (20 vol %) composite.
Elsewhere, less porosity is also observed in some composites. Indeed, this phenomenon is inherent to heterogeneous composite materials and is in good consistency with porosity results as presented elsewhere,\(^2\) where we have clearly explained that the decrease of porosity is achieved by filling the existing voids with filler loading as evidenced by density measurement, which was found to be steadily increasing with an increase in the loading.

Moreover, to test the surface roughness of our obtained composites, we have studied two samples, PbP/(Co,Cr) composites, using elemental mapping (EM) and energy-dispersive X-ray spectroscopy (EDX) spectroscopy. The results are shown in Figures 5 and 6.

Elemental maps of samples indicate the presence of Cr or Co (red dots) inside the PbP matrix.

Indeed, the element mapping by scanning electron microscopy and their corresponding EDX spectrum confirmed that the black areas in the studied composites represent voids. The metallic fillers are embedded inside the matrix by partially occupying the existing voids, and their distribution is almost homogeneous. We have to recognize that the previously performed sintering process also contributes to reducing the
porosity of the studied samples. Moreover, as displayed in both Figures 5 and 6, the EDS spectrum indicates traces of freestanding carbon and aluminum, which represent impurities, confirming the obtained results cited above.

Finally, the investigation of surface roughness by SEM mapping has clearly indicated fillers/matrix interfaces. The latter might lead to certain filler—matrix interactions, as shown above.

Metallic fillers play a role in reinforcement. Also, we have to obtain more features about the fillers/matrix interfaces that might influence many other intriguing physical properties of the elaborated composites. Therefore, we consider that surface energy calculations are of key importance, since they open a new window to the upcoming electrical and thermo-technical property modeling.

I.II. Contact Angle Measurements, Wettability, and Surface—Interface Energy Determination. I.III. Brief Theoretical Background. The angle $\theta$ formed by the intersection of the liquid—vapor interface and the liquid—solid interface is defined as the contact angle. Thus, three phases, solid, liquid, and vapor, coexist to form a "three-phase contact line". Thomas Young was the first to describe the contact angle $\theta$ of a liquid drop on a smooth, flat, and homogeneous solid surface defined by the mechanical equilibrium of the drop under the action of three interfacial tensions

$$\cos(\theta) = \left(\gamma_{LV} - \gamma_{SL}\right)/\gamma_{LV}$$

(1)

where $\gamma_{LV}$, $\gamma_{SV}$, and $\gamma_{SL}$ are interfacial tensions that measure the free energy (per unit area) of liquid—vapor, solid—vapor, and solid—liquid, respectively, and $\theta$ is the equilibrium contact angle. If we consider the measurements to be taken at the saturation pressure, eq 1 becomes

$$\cos(\theta) = \left(\gamma_{S} - \gamma_{SL}\right)/\gamma_{L}$$

(1a)

This relation clearly shows that the angle $\theta$ is determined by the ratio of the surface tensions. Thus, the shape of a liquid droplet is determined by the surface tension of the liquid.

Moreover, Table 1 shows that a small contact angle corresponds to good wettability. If the liquid is water, the solid surface is said to be hydrophilic. At the limit, when this corresponds to good wettability. If the liquid is water, the condition gives the shape of a sessile drop, pendant drop, or captive bubble. Contact angle often has been utilized to measure the hydrophobicity of the surface, since the wetting phenomenon is closely related to the free energies of the liquids and solids.

Relation 5 allows for the determination of the adhesion energy by the measurements of the contact angle. The same equation written as eq 6 shows that the contact angle represents the balance competition between the adhesion energy ($W_{SL}$) and the cohesion energy of liquid ($W_{LV}$).

I.III. Contact Angle Measurements. As noted above, the surface properties of solids are commonly investigated using the most widely used contact angle measurement technique, which later is determined between a liquid and a solid surface. Contact angle often has been utilized to measure the hydrophobicity of the surface, since the wetting phenomenon is closely related to the free energies of the liquids and solids.

Numerous techniques were carried out with the purpose to determine the contact angle and liquid surface tension, such as the shape of a sessile drop, pendant drop, or captive bubble. However, several researchers studied the surface free energies using the common method known as the sessile drop measurement. Thus, we are more interested in this method; we found it reliable and cheap to investigate the wettability of the
composites’ surfaces and calculate the surface and interface energies.

The measurements of contact angle were undertaken at ambient temperature through the placement of a liquid droplet with a syringe on the compacted composite discs of the four series containing metallic fillers with low, medium, and high incorporation levels (in volume fraction). To avoid the gravity effect, the droplet size of the liquid was about 3 μL. The discs of samples were polished and cleaned to obtain a flat, homogeneous, and smooth surface.

The wettability, surface energy, and interface matrix–filler energy of our elaborated composites have been determined using the process of Owens–Wendt.14

Then, the angle θ was calculated from the dimensions of the picture droplet, using the Analyzing Digital Images (software developed and freely distributed by STEM Education Institute, University of Massachusetts Amherst) and the following relation13

\[ \theta = 2 \arctan(2h/d) \]  
with: \( \theta < 90 \)  
where \( h \) and \( d \) represent the droplet’s height and length, respectively.

For more precision, the angle θ was also directly measured by capturing a recorded image of the liquid droplet profile of the droplet on a loaded lead glass matrix with a high-resolution CCD camera and using ScreenProtactor version 3.2 software of Iconico Inc., New York, NY.

II. RESULTS AND DISCUSSION

II.I. Composite Surface Water Wettability. First, it is important to signal that our investigation is limited to the static situation. The roughness, porosity, and heterogeneity of the surface is not taken into consideration.15–22 Hence, the kinetic effects22–24 are also not explored.

The SEM observations show that the surfaces of our samples are flat, homogeneous, smooth, and nonreactive. Therefore, we suppose that this is valid and take into account only the equilibrium state and apply the Young–Dupré equation.

Often, the materials of the devices during operation are subjected to humidity due to the presence of water. For this reason, we have limited our study of wettability under the effect of water (\( \gamma_d = 72.8 \text{ mJ/m}^2 \)). Thus, microdroplets of water were placed on composite samples. The observed contact angle was determined using the methods described above. The obtained water contact angle is lower than 90° for all samples. However, it increases when the filler amount increases, showing the hydrophobicity nature. It is obvious that the moderate observed wettability decreases with filler content, and the least values were observed at 40 vol %. This leads us to suggest that partial hydrophobicity occurs at a higher contact angle. Nevertheless, the measured contact angle is less than 90° for all samples, indicating that wetting of the surface is almost favorable. The work adhesion \( W_{SL} \) was determined using eq 5 and is given in Table 1.

It is clear that this energy decreases when the filler content increase, favoring the increase of the hydrophobicity of lead phosphate/metal composites.

This phenomenon can be understood using eq 6, indicating that the contact angle that measures wettability is the balance between adhesive and cohesive energies. Indeed, the cohesive surface energy of liquid (\( W^c = 2\gamma_L \)) due to the van der Waals attractive intermolecular forces, dispersive forces (London), polar forces (Keesom, Debye), or hydrogen bonds17 can be stronger than the force of adhesion attraction between the liquid molecules and the atoms in the solid (\( W^a = 2\gamma_{LL} > W_{SL} \)), and hence the liquid minimizes contact with the solid surface and forms a compact liquid droplet. Hence, the wetting of the surface is unfavorable. Elsewhere, the adhesion and cohesion energy balance expressed by eq 6 was also examined by De Gennes25 in terms of the surface polarizability (\( \alpha_L \)) ratio, originating in the attractive van der Waals interactions between the solid and liquid as

\[ \cos \theta = \frac{2\alpha_s}{aL} - 1 \]  

where \( \alpha_s \) and \( \alpha_L \) are the polarizabilities of the solid surface and liquid, respectively.

In our case, the used fluid is water, with a high surface tension of \( \gamma_d = 72.8 \text{ mJ/m}^2 \) or cohesion energy of \( W^c = 2\gamma_L = 145.6 \text{ mJ/m}^2 \). The hydrogen bond of water may increase the interaction of the hydrogen of water and the oxygen vacancies of the lead phosphate matrix favoring the wettability. Indeed, the role of oxygen vacancy in hydrophobic behavior was observed on titanium oxide (TiO\(_2\)) nanorods.26 Moreover, lead phosphate glass is known to be hygroscopic (likes water). This gives a contact angle θ of \( \approx 28° \). The determination of the solid surface tension of the neat lead phosphate matrix (PbP) gives \( \gamma_s = 53.42 \text{ mJ/m}^2 \). This value is somewhat high and according to eq 6 can lead to good wettability. However, when the surface of the matrix (PbP) is modified by loading with metallic fillers, the composite solid surface tension \( \gamma_s \) of all samples decreases continuously (see Table 1). The attraction of forces between the water molecules and the solid composite surfaces becomes lower than the cohesion forces of water (\( \gamma_s < \gamma_d \)). Hence, the surface develops hydrophobicity, and the wettability decreases, as seen in Table 1. Similar results were obtained on the PMMA/SiO\(_2\)–MgO composites, the polyurethane/clays nanocomposites, and the metallization of the polymethylpentene surface. The hydrophobicity increases notably on varying the filler amount or type, modifying the surface nature. Indeed, the modification of the material surface to obtain the desired wettability is actually an important industrial challenge. The wettability with water can be achieved by decreasing its tension surface (\( \gamma_s \)) by adding tension-active products or increasing the solid surface tension \( \gamma_s \) by modifying its surface by adsorption of organic polymers and surfactants.25 On the other hand, the nonwettability or hydrophobicity can also be obtained by a parallel process, which is by controlling the chemical nature by adding various additives, such as surfactants, sodium dodecyl sulfate (SDS),25 for example, and a coating process30,31 or physically by controlling the roughness32–35 of the solid surface (\( \gamma_s \)).

Such processes are very often used for hydrophobic or superhydrophobic surfaces in high-tech applications, such as photovoltaics requiring self-cleaning surfaces.32–35 In conclusion of this part, the study of the wettability by water of lead phosphate/metal composites showed that the loading of metallic fillers modifies the surface of materials. This effect lowered their solid surface tension (\( \gamma_s \)) and consequently favored their hydrophobicity. This result is important not only because the insulator phosphate products in the conducting materials are transformed but also because they become hydrophobic by loading it with metallic particles. Finally, the obtained results show a coherent behavior of wettability by natural modification of the elaborated composite surfaces, in good agreement with SEM observations, which revealed smooth and homogeneous surfaces.
II. Investigation of Fillers–Glass Interaction by Surface Energy Calculations. Fowkes\textsuperscript{66,37} was the first to propose that the surface energy due to the van der Waals forces, in condensed macroscopic media, can be expressed in its different components as

$$\gamma = \gamma^d + \gamma^p + \gamma^{ind} + \gamma^{11} + \ldots$$

(9)

where the subscripts d, p, ind, and H refer to dispersion (London forces), polar forces (Keesom, Debye), induction, and hydrogen bonds, respectively.

Then, Owens and Wendt\textsuperscript{14} proposed to group all components of surface tensions of the right-hand side terms of eq 9, except $\gamma^1$, in only polar interaction $\gamma^p$ as

$$\gamma = \gamma^d + \gamma^p$$

(10)

We use the equation of Girifalco and Good\textsuperscript{38} giving the interfacial solid–liquid interaction as

$$\gamma_{SL} = \gamma_s + \gamma_L - 2\Phi (\gamma_s \gamma_L)^{1/2}$$

(11)

where $\Phi$ often takes the value $\Phi = 1$

Combining eqs 10 and 11, Owens–Wendt\textsuperscript{14} and Kaelble\textsuperscript{39} obtained

$$\gamma_{SL} = \gamma_s + \gamma_L - 2(\gamma_s^{1/2} \gamma_L^{1/2} - 2(\gamma_s \gamma_L)^{1/2})$$

(12)

Using Dupré eq 3, we obtain the work of adhesion as

$$W_{SL}^a = 2(\gamma_s^{1/2} \gamma_L^{1/2} + 2(\gamma_s \gamma_L)^{1/2})$$

(13)

Combining eqs 4 and 13 gives

$$W_{SL}^a = \gamma_s (1 + \cos \theta) = 2(\gamma_s^{1/2} \gamma_L^{1/2} + 2(\gamma_s \gamma_L)^{1/2})$$

(14)

Owens–Wendt,\textsuperscript{14} Kaelble,\textsuperscript{39} and Rabel\textsuperscript{40} have written eq 14 in a linear form of the type $y = ax + b$ as

$$\frac{(1 + \cos \theta) \gamma_s}{2 \sqrt{\gamma_s}} = \sqrt{\gamma_p} \sqrt{x} + \sqrt{\gamma_s}$$

(15)

where

$$y = \frac{(1 + \cos \theta) \gamma_s}{2 \sqrt{\gamma_s}}$$

(16)

$$x = \sqrt{\gamma_s} \gamma_p \gamma_p \gamma_s$$

(17)

Equation 15 was used to determine the dispersive and polar components of $\gamma_s$ by measuring the contact angle $\theta$ and plotting $y = f(x)$. This method is well known as the Owens–Wendt–Rabel–Kaelble (WORK) method. Also, as can be seen, these measurements allow for the determination of the interfacial energies ($\gamma_{SL}$) using eq 12 and verifying the values of adhesion work ($W_{SL}$) using eq 13 of our phosphate glass/filler composite materials.

To determine the surface energy of composites, three liquids were used (distilled water, ethylene glycol, and glycerol) whose surface tensions and polar and dispersion components were known (see Table 2).

The surface energies of the PbP/metal composites and their components were determined versus filler volume fraction. The extracted data are compiled in Table 3.

### Table 2. Values of the Polar and Dispersive Surface Energies of Each Solution

| Solution       | $\gamma^p$ (mJ/m\(^2\)) | $\gamma^d$ (mJ/m\(^2\)) | $\gamma$ (mJ/m\(^2\)) |
|----------------|--------------------------|--------------------------|------------------------|
| glycol ethylen\textsuperscript{41} | 19.0                     | 26.4                     | 51.0                   |
| glycerol\textsuperscript{41} | 29.3                     | 37.0                     | 21.8                   |
| distilled water\textsuperscript{14,42,43} | 48.3                     | 63.4                     | 72.8                   |

### Table 3. Values of Total Surface Energy of Different Compositions Along with Their Polar and Dispersive Components

| Sample                  | $\gamma_s$ (mJ/m\(^2\)) | $\gamma^p$ (mJ/m\(^2\)) | $\gamma^d$ (mJ/m\(^2\)) | $\gamma$ (mJ/m\(^2\)) |
|-------------------------|--------------------------|--------------------------|--------------------------|------------------------|
| PbP/11 vol % Co         | 17.81                    | 6.92                     | 24.7                     |
| PbP/27 vol % Co         | 11.42                    | 0.88                     | 12.3                     |
| PbP/40 vol % Co         | 7.02                     | 0.10                     | 7.12                     |
| PbP/11 vol % Cr         | 19.18                    | 13.98                    | 33.16                    |
| PbP/27 vol % Cr         | 24.30                    | 0.42                     | 24.72                    |
| PbP/40 vol % Cr         | 13.76                    | 0.33                     | 14.09                    |
| PbP/11 vol % Ni         | 18.83                    | 7.84                     | 26.67                    |
| PbP/27 vol % Ni         | 10.31                    | 0.80                     | 11.11                    |
| PbP/40 vol % Ni         | 6.96                     | 0.03                     | 6.99                     |
| PbP/11 vol % Zn         | 12.67                    | 6.10                     | 18.77                    |
| PbP/27 vol % Zn         | 4.36                     | 0.75                     | 5.11                     |
| PbP/40 Vol % Zn         | 3.61                     | 0.00                     | 3.61                     |

Table 3 provides polar and dispersive components of the surface energies and the total surface energies of the phosphate glass matrix (PbP) and its composites. The results show that the solid surface energy of the matrix ($\gamma_s = 53.42$ mJ/m\(^2\)) is somewhat high and the dispersive component is dominant ($\gamma_s^d \gg \gamma_s^p$). This should be attributed to the cohesive energy ($W_{SL}^a = 2\gamma_s$) of covalent ($-P-O-$) and ionic ($-O-P-$) bonds inside the matrix. The polar interaction due to the (Pb\(^5\)–O\(^–\)) bond should be weak. However, the solid surface energy $\gamma_s$ values evidenced a significant decrease when the glass matrix was filled with metallic powders.

As can be seen, the minimal solid surface tension $\gamma_s$ is ascribed to 40 vol % in each of the four types of composites. Moreover, the polar contribution becomes important ($\gamma_s^p \gg \gamma_s^d$), and an inverse situation is observed. It seems that this phenomenon is linked to the attractive Van der Waals polar interactions between metals and the oxygen of the matrix. To confirm this assumption, we performed the measurements on polished filler discs. The results are given in Table 4. Indeed, the polar contribution is dominant in the surface tension of the metallic fillers. This effect may modify the surface composite chemical nature and increase the hydrophobicity, confirming the lowering of the wettability as found above with water. Indeed, the hydrophobicity increases continuously when the filler content loaded in the glass matrix increases, indicating a lowering of $\gamma_s$. This effect can be attributed to the surface modification by fillers. Such a surface change can be explained by the enhanced interfacial interaction ($\gamma_{SL}$) between the matrix and fillers when the filler loading increases, in good agreement with the observed behavior of SiO\(_2\)-MgO/PMMA composite films\textsuperscript{57} and polyurethane/clay nanocomposites.\textsuperscript{78}

This study shows that the inclusion of metallic fillers inside the insulator phosphate glass matrix plays an important role in the chemical structure of the obtained composites. This phenomenon seems to be related to the attractive interfacial filler–matrix interaction, which remarkably increases with filler contents.
leading to a decrease of the surface energy $\gamma_s$. As is known, $\gamma_s$ is related to the cohesion energy ($\gamma_s = W_s^r/2$). Thus, the surface energy $\gamma_s$ can be high for a particular hard solid, formed with covalent, ionic, or metallic bonds or low for weak crystals, like some polymers or liquids, bound by van der Waals intermolecular dispersive forces (London) or polar forces (Keesom, Debye) or by hydrogen bonds. Therefore, in our case, the metallic loading inside the lead phosphate glass matrix seems to alter the structure of chemical bonds, probably more at the surface. Therefore, the study of the moisture uptake behavior of fillers/glass composites and the effect of moisture on the surface properties is very important. Indeed, moisture is one of the important characteristic parameters of our studied composite surfaces and enables us to explain the tendency of interfacial adhesion.

To verify this assumption, a single sample was taken from each set of glass/metal composites. The four selected samples were then used to determine the water uptake. They were weighed directly after the sintering process. Then, they were placed under the same environmental moisture conditions. They were also weighed after different periods in high precision balances (accuracy of 0.1 mg). The water content of the samples can be calculated using eq 19 by taking into account the already calculated value of $\gamma_{mf}$ ascribed to the unloaded glass matrix (see Table 3). The loading of the glass matrix with metallic particles decreases its surface energy $\gamma_s$ and hence increases its alteration.

### II.III. Interfacial Interactions of the (PbP) Matrix and Filler Particles

The filler–matrix interfacial interaction energy $\gamma_{mf}$ can be estimated by writing eq 12 as

$$\gamma_{mf} = \gamma_m + \gamma_f - 2(\gamma_m^{d}\gamma_f^{d})^{0.5} - 2(\gamma_m^{p}\gamma_f^{p})^{0.5} \tag{19}$$

where $\gamma_m$ is the surface energy of the host matrix and $\gamma_f$ presents the surface energy of the filler, and the superscript $d$ and $p$ refer to the dispersive and polar components of the surface energy, respectively.

To calculate the interface energy between fillers and the host matrix, we measured the contact angle on polished filler discs using the same experiment and calculation methods described above to determine their surface energies and polar and dispersive components. The obtained results are depicted in Figure 7.

![Figure 7. Owens–Wendt–Rabel–Kaelble (OWRK) regression method determining filler surfaces.](https://doi.org/10.1021/acsomega.1c05314)

| Table 4. Weight Variation Record of PbP/Metal Composites in Air and the Calculation of Moisture Ratio |
|-----------------------------------------------|---------------------------------|-----------------|-----------------|
| samples | weight of the dry sample (g) at $t = 0$ | exposure time | weight after exposure in humid air (g) | moisture content (%) |
|---------|--------------------------------------|---------------|-----------------------------------|------------------|
| PbP/27 | 1.9391 | 24 h | 1.9391 | 0 |
| vol % Co | | | | | |
| day 7 | 1.9401 | | | 0.001 |
| day 15 | 1.9732 | | | 1.75 |
| day 30 | 2.074 | | | 6.95 |
| PbP/21 | 1.9340 | 24 h | 1.9340 | 0 |
| vol % Ni | | | | | |
| day 7 | 1.9386 | | | 0.237 |
| day 15 | 2.002 | | | 3.5 |
| day 30 | 2.0522 | | | 6.11 |
| PbP/23 | 0.7932 | 24 h | 0.7932 | 0 |
| vol % Zn | | | | | |
| day 7 | 0.7932 | | | 0 |
| day 15 | 0.8350 | | | 5.26 |
| day 30 | 0.8470 | | | 6.78 |
| PbP/19 | 2.2468 | 24 h | 2.2468 | 0 |
| vol % Cr | | | | | |
| day 7 | 2.2569 | | | 0.44 |
| day 15 | 2.3144 | | | 3.008 |
| day 30 | 2.3790 | | | 5.88 |
| day 45 | 2.4992 | | | 11.23 |

Therefore, the composite contact angles express higher values than that of the reference sample, confirming the obtained behavior presented in Table 3. The results are given in Table 4. It can be seen that the interface exchange energy between the matrix and fillers depends on the nature of the filler. It drops below the host matrix (PbP) value at room temperature, 53.42 mJ/m², and greater than that of the filler. This could probably be due to the

| Table 5. Dispersive and Polar Components Along with $\gamma_{mf}$ Values |
|-----------------------------------------------|-----------------|-------------|-----------------|
| fillers | $\gamma_f^d$ (mJ/m²) | $\gamma_f^p$ (mJ/m²) | $R^2$ | $\gamma_f$ (mJ/m²) | $\gamma_{mf}$ (mJ/m²) |
|---------|-----------------|-----------------|---|-----------------|-----------------|
| Co | 7.0 | 5.5 | 0.99 | 12.5 | 19.84 |
| Cr | 12.04 | 4.245 | 0.99 | 16.285 | 23.08 |
| Ni | 8.122 | 2.0 | 0.99 | 10.122 | 29.03 |
| Zn | 7.25 | 5.0 | 0.99 | 12.25 | 20.82 |

Then, the interface energy $\gamma_{mf}$ between the matrix and fillers was calculated using eq 19 by taking into account the already calculated value of $\gamma_{mf} = 53.42$ mJ/m² ascribed to the unloaded glass matrix (see Table 3). The results are given in Table 5. It can be seen that the interface exchange energy between the matrix and fillers depends on the nature of the filler. It drops below the host matrix (PbP) value at room temperature, 53.42 mJ/m², and greater than that of the filler. This could probably be due to the
coating process of the filler by the matrix. Hence, the interface is dominated by matrix contribution to the surface exchange. Studies conducted on some composites have shown quite similar findings.\textsuperscript{18,39}

## CONCLUSIONS

The aim of the present thesis work is to prepare binary phosphate glass-based composites in bulk form (PbP/Co, Cr, Ni, or Cr) and study their surface and interface properties through corroborating scanning electron microscopy and contact angle measurements. To investigate the glass–filler interactions within the elaborated composites and evaluate the quality of their surfaces, it was necessary to conduct contact angle measurements. The wettability, surface energy, and interface matrix–filler energy of the investigated composites have been determined using the process of Owens–Wendt. The image of the droplet was taken with an external CCD camera connected to a computer. The obtained water contact angle is lower than 90° for all samples. However, it exhibits an increase when the filler amount increases, showing the hydrophobicity nature. It is obvious that the moderate observed wettability decreases with filler content, and the least values were observed at 40 vol %.

A good correlation between contact angle measurement and surface morphology was made since the contact angle is highly influenced by the surface quality. Indeed, contact angle measurements on our composite's materials are coherent. It is a free-of-cost- and reliable tool for determining surface energy, since surface and interface energy play an important role in possible industrial applications. Moreover, the determined interfacial surface energy $\gamma_{\text{int}}$ will be used in further electrical conduction modeling.

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### Notes

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