ANALYSIS OF POLYMER/METAL INTERACTION FOR OBTAINING RELIABLE ELECTRONIC DEVICES

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Abstract: *Some polymers of great importance in electronic industry were investigated with respect to their surface features in view of evaluation of metal adhesion. The structural characteristics, which are typical to each studied material, determined different values of the metal work of spreading. The variations in surface polarity affected the adhesion interactions between polymer and inorganic phase. The results bring new information on the manner in which polymers should be used in electronics in order to increase stability of the joints in circuits and implicitly the device reliability.*

Keywords: *polymer, surface properties, metal interaction*

1. Introduction

The rapid development of electronic devices in microelectronics leads to more intensive use of combination between metallic compounds and polymers [Nguyen, 2016]. Various types of polymers are selected to fulfill the operating conditions of the adhesive joint and to be able to bond properly to a metal coat, the most known being polyimides, polystyrene, polysulfones, etc. Conversely, certain metals like gold, silver, aluminum or copper are commonly found in electronic pieces, being necessary to join with other materials, especially polymers. Therefore, the polymer/metal interface becomes an important parameter in designing these systems, the main concern being to optimize the adhesion strength.

During last decades, many attempts have been performed on the enhancement of adhesion strength and long-term stability of polymer/metal interfaces under different environmental conditions [Albu, 2014]. Thus, it is essential to elucidate the phenomena that appear at the joints. In this manner, one may achieve supplementary information on the reliability of the electronic device. So, polymer/metal interface are analyzed in detail since both types of materials are frequently encountered in devices because they represent ideals for dielectric and conductors, respectively [Ruschau, 1992].

The present work attempts to provide a deep investigation on the interactions that occur at the polymer/metal interface. Several types of polymers used in electronics are introduced in this analysis. They are selected on the basis of their distinct chemical structure that determines a different set of physical properties. Thus, polymers containing imidic rings or sulfone groups are known as materials that are resistant at high temperatures. Fluorine-derived polymers exhibit low polarizability and consequently low dielectric constant combined with smaller glass transition temperature. The interaction of these compounds with some basic metals, which are often used in designing electronic circuits, is determined. This was made for some samples based on their surface wettability properties. In this manner, the spreading work of metal on the polymer support can be assessed. On the other hand, the interactions with metals can be determined by evaluation of interaction potential energy of each phase. The obtained results have a great impact in designing components with optimal interfacial interaction, thus augmenting the feasibility of electronic devices.

2. Experimental

The macromolecular compounds selected for this investigation are represented by different classes of high performance polymers, such as namely polyvinylidene fluoride (PVDF), quaternized polysulfone (PSF), polyimide (PI) and poly(4-vinylpyridine) (P4VP). Each of these materials have different dielectric behavior and surface properties in terms of polarity as a result of the chemical structure peculiarities.

The metals used in this study are gold (Au), silver (Ag) and aluminum (Al). They are widely used in construction of conducting elements of electronic circuits.

The surface properties of each material selected for investigation were determined through contact angle method. The corresponding measurements were previously reported [Ioan, 2011; Buruiana, 2015; Cosutchi, 2008; Raczkowska, 2016; Soroceanu, 2017]. The surface tensions of the polymers considered here are listed in **Table 1**.

Table 1: The surface tension components of the studied polymers.

Polymer	γ^d	γ^p	γ^{total}
PSF[a]	39.60	2.95	42.55
PVDF[b]	22.10	0.60	22.70
PI[c]	38.83	7.71	46.54
P4VP[d]	36.30	3.30	39.60

[a] taken from [Ioan, 2011]; [b] taken from [Buruiana, 2015]; [c] taken from [Cosutchi, 2008]; [d] taken from [Raczkowska, 2016]

3. Results and discussion

In this work, the data concerning the surface tension are further processed in order to determine the interactions occurring at the interface of these polymers when they faced with metals. The degree of surface polarity or dispersity (London forces) of the polymer and inorganic particles has a great influence on the binding ability of both materials [Owen, 2000]. The balance between adhesion and cohesion forces acting at the interface is best described by a parameter that accounts on polar and disperse components of surface tension of the two phases [Lee, 1991]. Thus, in this study the spreading work of the metal on polymer support is calculated with the following formula:

$$W_s = W_{adhesion} - W_{cohesion} \quad (1)$$

$$W_s = 2\left(\sqrt{\gamma_p^{disp} \cdot \gamma_m^{disp}} + \sqrt{\gamma_p^{pol} \cdot \gamma_m^{pol}}\right) - 2\gamma_m \quad (2)$$

where W_s is the work of spreading, γ is the surface tension, the subscripts "p" and "m" denote the polymer and metal phase, and the superscripts "disp" and "pol" indicate the disperse and polar components of surface tension.

The interfacial polymer/metal tension (γ_{p-m}) was evaluated using equation (3):

$$\gamma_{p-m} = \left(\sqrt{\gamma_m^{pol}} - \sqrt{\gamma_p^{pol}}\right)^2 + \left(\sqrt{\gamma_m^{disp}} - \sqrt{\gamma_p^{disp}}\right)^2 \quad (3)$$

Interfacial free energy between two particles of polymer in metal phase (ΔG_{p-m-p}) is described by relation (4):

$$\Delta G_{p-m-p} = -2 \cdot \gamma_{p-m} \quad (4)$$

The surface tensions of each material that is interfaced have great implication on the work of spreading. **Table 2** shows the results obtained for analyzed polymers and the three considered metals.

Table 2: The values of the work of spreading of the three metals on the studied polymers.

Polymer	W_s		
	Au	Ag	Al
PSF	-1.87	-2.71	-9.72
PVDF	-25.59	-26.95	-34.42
PI	0.94	0.86	-1.56
P4VP	-4.99	-5.78	-11.74

Given the different structural features of the macromolecular compounds, one may observe that the spreading ability is not the same for all metals. Thus, PSF is better coated by Al, PVDF and P4VP are covered easily by Au, whereas PI has a preference for both Au and Ag.

On the other hand, for a certain metal, one may notice in **Table 2** that highest work of spreading is occurring for PI and PSF samples. In case of PI/Au and PI/Ag interfaces, we have obtained the highest work of spreading. The positive values obtained for these two situations reveal the fact that the metal in contact with polyimide interacts prevalently through adhesion forces and less cohesion ones. For the other polymers, here under analysis, the negative values for W_s indicate preponderant cohesion interactions at the interface.

Another parameter that could provide information on the compatibility between the two types of materials is the interfacial polymer/metal tension. The resulted values are listed in **Table 3**.

Table 3: The values of interfacial polymer/metal tension.

Polymer	γ_{p-m}		
	Au	Ag	Al
PSF	0.02	0.125	6.96
PVDF	3.89	4.52	11.81
PI	1.19	0.55	2.79
P4VP	0.19	0.20	6.03

It can be remarked that as the interfacial tension is lowered (particularly for P4VP, PSF and PI) the compatibility with the inorganic phase is enhanced for all considered metals. Analyzing the mean values of the interfacial tension of samples with these metals one can distinguish the following inequality for γ_{p-m}: Ag ≤ Au < Al. Therefore, these macromolecular compounds have increased compatibility with components made by Au or Ag, and less with Al.

The data achieved for interfacial free energy between two particles of polymer in metal phase are presented in **Table 4**.

Table 4: The **i**nterfacial free energy between two particles of polymer in metal phase.

Polymer	ΔG_{p-m-p}		
	Au	Ag	Al
PSF	-0.04	-0.25	-13.93
PVDF	-7.79	-9.04	-23.61
PI	-2.39	-1.10	-5.59
P4VP	-0.37	-0.39	-12.05

The negative values for this parameter reflect a good attraction between polymer surface and all three metals.

The adhesion interactions were estimated from the surface energy properties of both materials. The work of adhesion is influenced by the ratio between the polar and dispersive contributions to the total surface tension of the analyzed materials. **Figure 1** displays the results regarding work of adhesion as a function of polymer surface polarity.

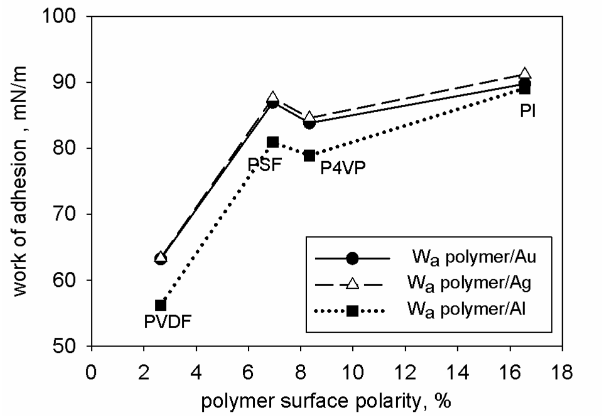

Figure 1: The values of work of adhesion as a function of polymer surface polarity.

Regardless the considered metal, the adhesion work ranges in the following order: PI > PSF > P4VP > PVDF. This can be explained on the basis of sample structure. Polyimides exhibit good adhesion properties owing to the imide moieties in their backbone. The polysulfone, here under investigation, has a quaternized structure that involves supplementary electrostatic interactions, which favor adhesion interactions with metal. P4VP maintains this property at a similar level with PSF probably due to its polar nature of pyridine rings. Conversely, PVDF has a low mean polarity because of the presence of fluorine atoms, which present an electron-withdrawing character.

All macromolecular specimens give the same variation for the work of adhesion with metals: Ag > Au > Al. This means that silver/polymer joint are recommended for electronic applications.

4. Conclusions

Four polymers with different structure were evaluated in regard with their surface properties. The interactions with three metals were assessed based on surface tension characteristics. Several parameters were estimated in order to determine the optimal interactions at the polymer/metal interface. The chemical structure of the macromolecular compounds determined a specific surface polarity. The latter influenced the adhesion and spreading ability of metal on the polymer specimens. The obtained data indicated that the best compatibility was achieved for Ag or Au polymer joints, while from the point of view of the organic phase PI and PSF are most desirable. These two polymers are good candidates for utilization in manufacturing dielectric components for electronic circuits owing to their optimal adhesion with metals.

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