A STUDY REGARDING THE SURFACE PROPERTIES OF RUBBERS-BASED ADHESIVE ASSEMBLIES

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În această lucrare sunt calculate şi interpretate valori ale unor parametri ai procesului de adeziune utilizând soluţii de cauciuc: tensiunea superficială la interfaţa solid-lichid, lucrul de udare şi lucrul de adeziune, concentraţia superficială şi suprafaţa ocupată de o moleculă de elastomer. Valorile au fost obţinute din date experimentale ale tensiunii superficiale şi unghiului de contact. Soluţiile investigate au conţinut cauciuc natural, cauciuc policloroprenic şi cauciuc butadien-nitrilic dizolvat în solvenţii organici specifici (benzina de extracţie , toluen şi metil-etil-cetonă) în domeniul de concentraţii 12-25 % în greutate.

In this paper, based on the experimental data of surface tension of rubber solutions and contact angle, the values of some parameters involved in adhesion process, as solid-liquid surface tension, work of wetting, work of adhesion, superficial concentration and surface area occupied by an elastomer macromolecule were computed and interpreted. The investigated adhesive solutions contained natural rubber, polychloroprene rubber and nitrile butadiene rubber dissolved in appropriate organic solvents (gasoline, toluene and methyl-ethyl-ketone, respectively) in concentration range of 12-25 wt. %.

Keywords: adhesive solutions, surface tension, natural rubber, polychloroprene rubber, nitrile butadiene rubber

1. Introduction

The adhesion phenomenon is the subject of many researches aiming at finding a unitary theory of the adhesion process. Based on these studies, several theories on the adhesion process have been issued: the theory of diffusion, adsorption theory, electric theory, chemisorption theory, as well as mechanical models theory [1-7]. Nevertheless, all these theories have limits [8]. In the specialty literature, the adhesion is considered rather as a chemical interfacial phenomenon instead of physical surface phenomenon. This is why many papers

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have been dedicated to study the interface role on the polymer-substrate bond [10-14].

In the previous works [15,16], there were presented our researches on adhesion of non-polar vulcanized elastomer assemblies using non-polar solutions as adhesives; also, the adhesion of polar vulcanized elastomer assemblies used as adhesive solutions was investigated. In this paper, based on the previously obtained experimental data [15,16], the values of some parameters involved in adhesion process, as surface tension, work of wetting, work of adhesion and superficial concentration and surface area occupied by an elastomer macromolecule were computed and interpreted.

2. Experimental

The surface tension of the solutions was determined by Wilhelmy method [5]. The Wilhelmy method consists in the determination of the force of the liquid meniscus when a glass plate has the inferior edge at the same level with the surface of the liquid as shown in figure 1.
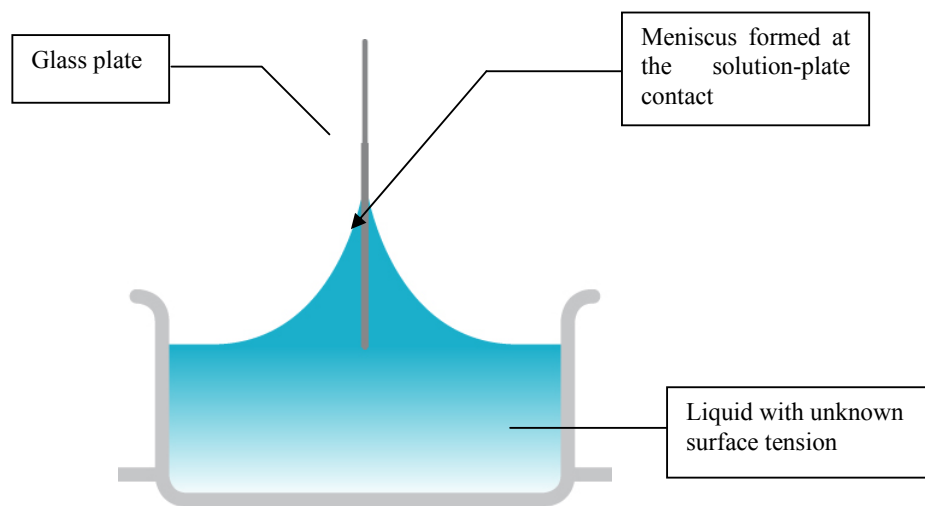

Fig.1. Principle of Wilhelmy method to measure the surface tension

The liquid vessel is raised with a micrometric knob to reach the plate suspended on a weighing balance. At this moment a sudden up and down vibration movement appear due to the formation of the liquid meniscus. Practically, the plate is immersed in the adhesive solution placed in a recipient on the weighing balance. The Wilhelmy method recommends the use of platinum,

mica or glass plates. The experiments presented in this work were carried out on a glass plate (25×25×1.3 mm).

The surface tension value was computed with the following equation:

$$\gamma = \frac{mg}{2(l_1 + l_0)} \tag{1}$$

where:

mg – force of the liquid meniscus against the length of the plate perimeter (m is the equivalent weight and g is the gravitational acceleration)

l_1 – length of the plate

l_0 – correction parameter (end scale error) equal to the thickness of the plate

Each experiment was done in triplicate and the results are expressed as arithmetical average values.

KSV CAM 101 goniometer was used for measurements of static contact angle, performed on dried films. The measurement of each contact angle was made within 10s time interval after dropping each droplet on the solid surface, to ensure that the droplet did not soak into the compact state. The contact angles reported were an average of four identical determinations.

The investigated adhesive solutions were the followings:

- natural rubber solutions, with gasoline as solvent, having the concentrations of natural rubber *(L1100)* ranging from 12.7% to 25%;
- polychloroprene rubber solutions, with the polychloroprene rubber *(CR1)* dissolved in toluene in concentrations ranging from 20 to 25%;
- nitrile butadiene rubber solutions (AZ4) obtained by dissolving nitrile butadiene rubber in methyl-ethyl-ketone in concentrations ranging from 16 and 20%.

The tested adhesive solutions contained also vulcanization groups, specific to each type of elastomer and the corresponding antioxidants [15, 16].

3. Results and discussion

The surface tension is an important parameter of an adhesive solution being a measure of the uncompensated cohesion forces from the surface of a liquid in contact with its vapours. It can be also defined as a force that acts against the length of the separation perimeter, oriented towards decreasing surface. The contact angle is a proof of compatibility between two materials, which could accept each other and form adhesive assemblies. Smaller contact angles correspond to an increased wettability. In our experiments we tried to test if the solutions of natural rubber, polychloroprene rubber and nitrile butadiene rubber dissolved in organic solvents (gasoline, toluene and methyl-ethyl-ketone, respectively) may be used as adhesive solutions because of their adhesion property.

The surface tension at a solid-adhesive liquid interface (γ_{SL}) has a main role in the adhesion process for joining of two solid bodies. Computation of this solid-liquid surface tension may be performed using Young-Dupré equation [8, 9)] and known values of the liquid-gas surface tension (γ_{LG}) of adhesive solution and solid-gas surface tension (γ_{SG}):

$$\gamma_{SL} = \gamma_{SG} - \gamma_{LG} \cdot \cos\theta \qquad (2)$$

In the eq. (2), θ is the contact angle (degrees), which has the significance of a wetting angle.

Table 1

The calculated values of solid-liquid surface tension (γ_{SL}) for the solutions used as adhesives

Rubber concentration, wt. %	θ, degrees	γ_{SG} x10³, N/m	γ_{LG} x10³, N/m	γ_{SL} x10³, N/m
Natural rubber solution (L1100)				
25	83	31	31.46	27.17
22.3	73	31	29.06	22.50
20.8	67	31	26.91	20.49
12.7	58	31	24.28	18.13
Polychloroprene rubber solution (CR1)				
25	72	38	26.25	29.89
22.3	68	38	25.65	28.34
20.8	41	38	24.14	19.78
Nitrile butadiene rubber solution (AZ4)				
20	70	37	30.24	26.66
17.1	68	37	29.28	26.03
16.6	65	37	28.25	25.06

Table 1 shows the values of solid-liquid surface tension (γ_{SL}) for all three investigated solutions, calculated using equation (2) together with the experimental data of γ_{LG} and θ. The $\gamma_{critic\ SG}$ values reported in literature (0.031 N/m for natural rubber, 0.038 N/m for polychloroprene rubber, 0.037 N/m for nitrile butadiene rubber [8, 9] are also given.

Based on the data shown in Table 1, the spreading coefficient S may be calculated:

$$S = \lambda_{SG} - \gamma_{SL} - \gamma_{LG} \qquad (3)$$

where λ_{SG} is the solid-liquid surface tension.

The values of the spreading coefficient are negative for all the solutions investigated, meaning that the adhesive solutions do not scatter onto the substrate.

Based also on the results shown in Table 1, the values of work of wetting, W_w and work of adhesion, W_a for the surface area equal to unity ($1m^2$ may be computed using the following equations [9]:

$$W_w = \gamma_{LG} \cdot \cos\theta \qquad\qquad\qquad (4)$$

$$W_a = \gamma_{LG}(1 + \cos\theta) \qquad\qquad\qquad (5)$$

The results of calculated values for W_w and W_a are listed in Table 2.

Table 2

Values per $1m^2$ surface area of the work of wetting and work of adhesion for the investigated adhesive solutions

Rubber concentration, wt. %	γ_{LG} x10^3, N/m	W_w x10^3, J (per $1m^2$ surface area)	W_a x10^3, J (per $1m^2$ surface area)
Natural rubber solution (L1100)			
25	31.46	3.83	35.29
22.3	29.06	8.50	37.56
20.8	26.91	10.51	37.42
12.7	24.28	12.87	
Polychloroprene rubber solution (CR1)			
25	26.25	8.11	34.36
22.3	25.65	9.59	35.25
20.8	24.14	18.20	42.33
Nitrile butadiene rubber solution (AZ4)			
20	30.24	10.34	40.59
17.1	29.28	10.97	40.25
16.6	28.25	11.94	40.16

By comparing the data from Tables 1 and 2 it may be noticed that the work of adhesion per surface area unit is higher than the liquid-gas surface tension, a fact that is very important in the adhesive assemblies. Taking into account the classification of solids as function on values of surface tension and wetting angle (see the scheme in Figure 2), the existence of a region of the solids with wetting properties and high energy describes our situation. This proves that the solid-liquid molecular attractions are stronger than liquid-liquid attractions.
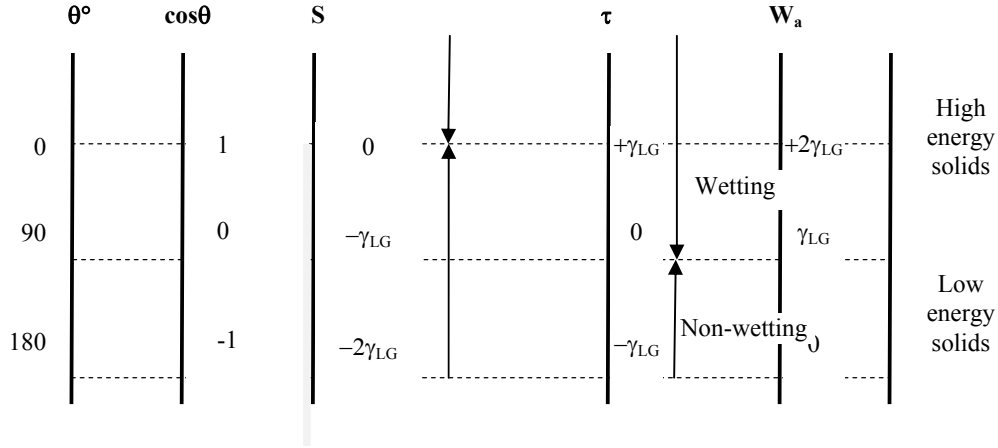
Fig.2. A classification of solids according to surface tension and wetting angle

In his paper, Zisman proposed the following equation for the meniscus radius from a capillary filled with liquid [17]:

$$r = \frac{(\cos\theta - 1)}{(\gamma_{criticSL} - \gamma_{LG})} \tag{6}$$

According to our experimental data (see Table 1), we found that the value of the meniscus radius for the solution with 25% natural rubber is positive:

$$r = \frac{(\cos 83 - 1)}{(31 - 31.46)} = 1.9 cm \tag{7}$$

For any other elastomer and concentration of adhesive solutions (even for natural rubber solutions), the calculated values of the meniscus radius were negative. This means that in those cases the adhesive solution does not enter the capillaries. As a consequence, the attack takes place only at the surface where the adsorption of the adhesive macromolecules develops.

Related to adsorption process that is involved in the adhesion, the superficial concentration (Γ) of rubber when the solution is spread onto the solid surface may be defined as:

$$\Gamma = \frac{n^S}{A} \tag{8}$$

where n^S=number of adhesive moles per active surface unit, and A=active surface area of the solid.

Taking into account the values of the molecular weights of the elastomers dissolved in the adhesive solutions (38000, 100000, 120000 g/mole for natural

rubber, polychloroprene rubber and nitrile butadiene rubber, respectively the amount of rubber and the active surface of the test samples (37.5 cm^2) used in our experiments, the superficial concentrations Γ of rubber was therefore computed. Furthermore, the obtained Γ values allowed the estimation of the surface A* occupied by each elastomer molecule when the adhesive solution was spread onto the surface:

$$A* = \frac{1}{N_A \cdot \Gamma}$$
(9)

where N_A=Avogadro's number, Γ=superficial concentration.

Table 3 shows the obtained data for Γ and **A*** parameters.

Table 3

The superficial concentration (Γ) and surface (A*) occupied by an elastomer molecule from the adhesive solution

Rubber concentration in adhesive solution, wt. %	Amount of elastomer, g	Moles of elastomer onto 37.5 cm^2 surface, $\times 10^5$	Superficial concentration (Γ), moles/cm$^2 \times 10^6$	A*, Å^2
Natural rubber solution (L1100)				
25	4.69	12.3	3.28	0.506
22.3	4.18	11.0	2.93	0.566
20.8	3.90	10.2	2.72	0.610
12.7	2.38	6.2	1.65	1.001
Polychloroprene rubber solution (CR1)				
25	8.44	8.44	2.25	0.007
22.3	7.53	7.53	2.00	0.008
20.8	7.02	7.02	1.87	0.009
Nitrile butadiene rubber solution (AZ4)				
20	1.50	1.25	0.33	0.050
17.1	1.28	1.07	0.29	0.058
16.6	1.25	1.04	0.28	0.061

The graphical representation of the surface tension of adhesive solutions versus concentration (Fig. 3) gives important information about the behaviour in the adhesion process.
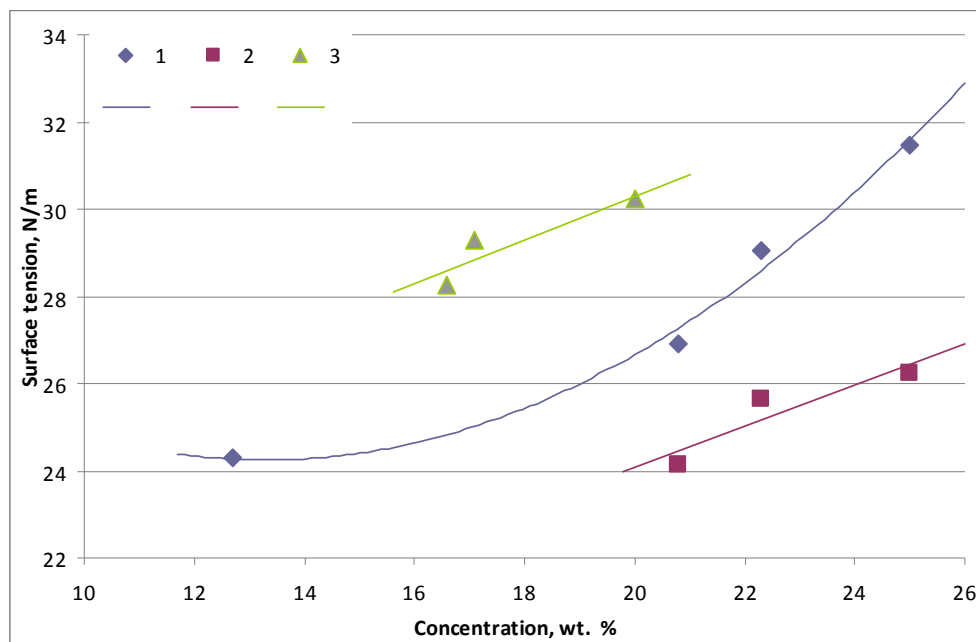
Fig. 3. Surface tension versus rubber concentration dependence for investigated adhesive solutions; 1 – natural rubber solution; 2 – polychloroprene rubber solution; 3 – nitrile butadiene rubber solution

As can be seen in the above figure, the solution of natural rubber has a poor tension-active behaviour, a fact that was also proved by the weak adhesive properties within the peeling test [1]. The better adhesive characteristics of polychloropren rubber may be associated with its colloid-type behaviour [18]. In this case, the behaviour with respect to solid adsorbent is strongly influenced by the existence of the polar halogen group, which induces the polarization of the double group within the macromolecule structural unit. In the case of butadiene-nitrile rubber, the surface tension of its adhesive solution varies linearly with rubber concentration proving relatively weak tensioactive-type behaviour.

According to the values presented in Tables 1 and 3, the surface tension increases with the concentration of the solution, but the surface area occupied by a macromolecule in the superficial layer decreases. This experimental result may show that the decrease of the space occupied by a rubber macromolecule within the superficial layer has a negative influence upon the adhesion resistance.

The adsorption isotherms (Γ–c dependences) drawn for all three adhesive solutions investigated (see data in Table 3) are straight lines with positive slopes. These adsorption isotherms prove the high compatibility between the solid adsorbent and adsorbed species.

4. Conclusions

The experimental determinations of the surface tension of the elastomer solutions used as adhesives between two solids, as well as computation of the work of adhesion and surface area occupied by a macromolecule revealed the following aspects:

- All rubbers dissolved in appropriate organic solvents behave as surface active substances; the surface tension for liquid./solid interface increase with concentration of rubber in adhesive solution. The value of the scattering coefficient is almost always negative meaning that the droplets of adhesive solution do not scatter (spread) onto the substrate.

- The determination of the work of adhesion for three investigated rubber solutions indicates that we can frame the liquid/solid interface into the domain of high energy (according to Zisman's theory of adhesion), where the molecular attraction of the solid to the liquid is higher than own molecules of liquid phase.

- The study of the influence of the rubber concentration on the surface tension revealed poor tension-active behaviour for natural rubber, associated colloid-type behaviour as well tension-active substance for polychloroprene rubber and relatively weak tension-active behaviour for nitrile butadiene rubber. The adsorption isotherms prove the good compatibility between the adsorbent (solid) and adsorbed liquid (adhesive solution).

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