Comparative Analysis on the Performances of the Pressure Sensitive Adhesives based on Polychloroprene Rubber and Hybrid Acrylic Adhesives

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The paper presents a comparative analysis between the performances of pressure sensitive adhesives based on polychloroprene rubber and hybrid acrylic adhesive. The analysis was based on peel, shear and tensile tests for the assemblies on various substrates. Adhesion work was also determined from the contact angles and superficial tensions. The values of the adhesion work confirm the results obtained with the above mentioned tests.

Keywords: pressure sensitive adhesives, polychloroprene-based rubber, hybrid acrylic adhesives

Pressure sensitive adhesives are a class of very important adhesives that adhere to various substrates when applied under pressure. Their adhesion to substrate is not chemical or mechanical, but a polar attraction towards the substrate surface. Pressure is required for an efficient wetting of the substrate surface and correspondingly a good adhesion. Pressure sensitive adhesives do not need water, solvent or temperature for activation [1-4]. These additives have found applications in constructions, electronic industry, aeronautics, automotive industry, medicine and dentistry, packaging industry (food labels, adhesive bands for sealing an fixation).

Pressure sensitive adhesives contain carbocatenary elastomers, modified acrylic polymers or silicon rubbers [4-5].

Two the most used carbocatenary elastomers are polychloroprene and butadiene-styrene rubbers. Polychloroprene rubber is a polar elastomer with many uses for the obtaining of pressure sensitive adhesives and high performance structural adhesives.

Hybrid acrylic adhesives represent a new class of pressure sensitive adhesives, which combine the performances of acrylic adhesives with those based on elastomers [7-13].

Combining the performances of the two types of adhesives was done by the obtaining of grafted copolymers, in which the main chain is polyacrylic and the grafts are saturated hydrocarbons with 2000-3000 g/mole molecular weight and -20-(-50)°C glass transition temperature (typical elastomeric behaviour) [14].

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Experimental part

Materials and methods

An adhesive solution (composition in table 1) and a hybrid acrylic adhesive obtained by the copolymerization of ethylene-propylene macromer with methacrylic end groups (2-ethyl-hexyl acrylate and acrylic acid) were used. The hybrid acrylic adhesive is named Duro-Tak® AH100 provided by National Starch and Chemical Company, Adhesives Division, USA.

Table 1
COMPOSITION OF THE ADHESIVE SOLUTION BASED ON POLYCHLOROPRENE RUBBER; THE FINAL SOLUTION CONCENTRATION 20%; THE SOLID CONTENT OF THE FINAL SOLUTION IS 25%

No.	Material	Concentration, %	Role in the recipe
1	Polychloroprene rubber (Denka A90)	100	Elastomer
2	Hydrogenated colophonium	10	Sticking agent
3	2,6-di-t-butyl-4-methyl-phenol (BHT IONOL)	2	Antioxidant
4	MgO	8	Active filler
5	ZnO	5	Active filler
6	Toluen	375	Solvent

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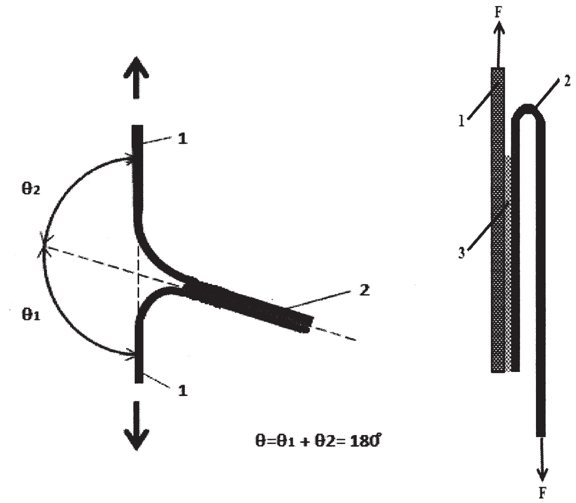

Fig.1. Peel test (T-peel)
A) Adhesive assemblies between flexible substrates
1-flexible substrate; 2-adhesive layer
B) Mixed adhesive assemblies between rigid and flexible substrates 1-rigid substrate; 2-flexible substrate; 3-adhesive layer

Various types of samples were used to determine the mechanical strength of the adhesive assemblies. The peel strength was determined on adhesive assemblies between rigid substrates (parallelipipedic samples 100 x 25.4x1.4 mm for 2024 T_3 duralumin, Royalite (PVC), Textolite, steel and aluminium; samples of 120 x 25.4 x 4 mm for PMMA), flexible substrates made out of plasticized PVC on textile support, assemblies between flexible substrates (plasticized PVC on textile support) and adhesive assemblies between rigid substrates.

The adhesive was applied in one layer both on rigid and flexible substrate. After complete solvent evaporation the two substrates were bonded and maintained under a certain pressure for a predefined contact time.

The peel test was performed on a Universal Testing machine INSTRON 3382 under 180° angle (T-peel test) [15-17], (fig. 1).

Shear strength was determined on the above mentioned rigid samples by applying the adhesive in one layer on a surface of 25.4x25.4 mm. The samples were bonded by lap joint and maintained under a certain pressure for a predefined contact time. The shear strength was performed on a Universal Testing machine INSTRON 3382.

The tensile strength was determined on adhesive assemblies between cylindrical samples made out of oak tree wood or steel on the same Universal Testing Machine.

For all the measurements, before applying the adhesive onto the substrate, the samples were conditioned by solvent degreasing (isopropanol, acetone or methyl-ethyl ketone). Before degreasing, the rigid samples were polished with a very thin sand (60G granulation), and the duralumin 2024 T_3 samples were etched with sulpho-chromic mixture.

Measurements of superficial tension were performed on a torsion balance by ring detachment from the surface of the analyzed liquid (Du Nöuy method). The suspended platinum ring is weighed together with the platinum wire. The ring characteristics are the following ones: radius of the platinum wire (r=0.25 mm) and the radius (R) measured from the centre of the ring to the middle of the circular wire (R=10 mm). The free balance arm was loaded with 80% of the required weight to detach the ring. The ring was kept onto the surface of the liquid for 1 minute to reach the superficial equilibrium. The torsion balance was used to ensure the necessary force for ring detachment. The difference m between the weight required to detach the ring and its weight in air allows the determination of the superficial tension γ according to the equation:

$$\gamma = \frac{mg}{4\pi R} \cdot F \qquad (1)$$

where g is the gravitational acceleration and F a correction factor (Harkins and Jordan) that takes into account the volume levelled by the ring and the difference between the ring radius R and the actual radius of the meniscus in the breaking plane [18-20]. The correction factor F is determined based on the ratios R^3/V and R/r, where V is the maximum total liquid volume from the meniscus (over the surface). Volume V is calculated for each determination as the ratio between the total weight necessary for ring detachment and liquid density ($V=m/\rho$). The densities of the adhesive solutions were determined with the picnometer at 25°C.

For each of the two adhesive solutions 10 determinations were made for the total weight m; the average value was computed and according to equation (1) the superficial tension.

The average values for the superficial tensions and the corresponding standard deviations are shown in table 2.

The determination of contact angle [21-22] between the adhesive solutions and the rigid substrates was done on a Contact Angle meter-KSV Instruments CAM 100. The values are shown in table 3.

Results and discussions

The studies on the adhesive characteristics of the pressure sensitive systems based on polychloroprene rubber and hybrid acrylic adhesive revealed a series of resemblances and differences between the two systems.

The peel strength is the main characteristic of the pressure sensitive adhesives. The contact time, contact pressure and substrate nature are the main factors that influence the peel strength. The determinations for the peel

Table 2
VALUES OF THE SUPERFICIAL TENSIONS AND THE CORRESPONDING STANDARD DEVIATION

No.	Adhesive	P, g/mL	Superficial tension, mN/m	Standard deviation, mN/m
1	Polychloroprene adhesive	0.9241	29.639	0.13916
2	Hybrid acrylic adhesive	1.008	31.288	0.20938

No.	Substrate	Contact angle (θ), degrees	
		Polychloroprene rubber solution	Hybrid acrylic adhesive
1	Textolite	53.59	85.74
2	Royalite (PVC)	56.40	86.05
3	Polymethyl methacrylate	59.44	86.39
4	Aluminium	54.20	79.97
5	Al alloy	58.59	81.4
6	Steel	62.43	89.26

Table 3
VALUES OF THE CONTACT ANGLES FOR DIFFERENT SUBSTRATES

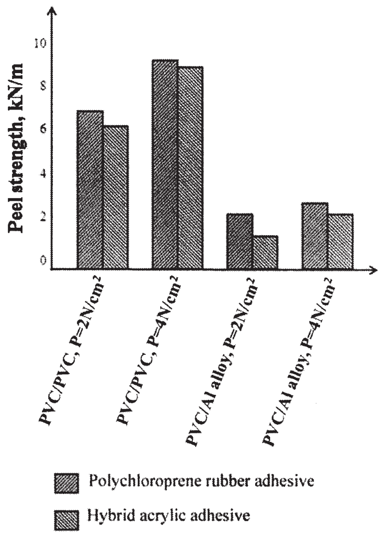

Fig.2. Influence of the pressure on the peel strength

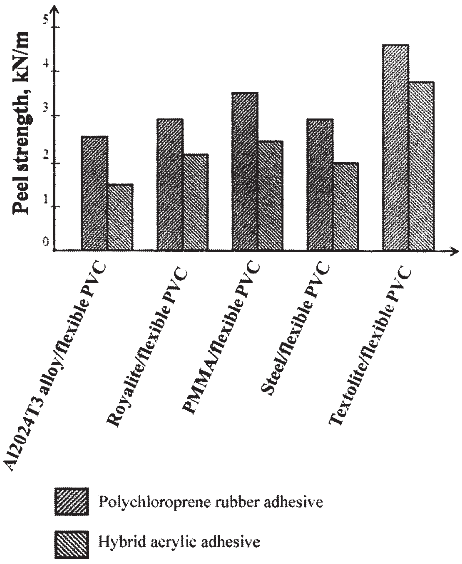

Fig.3. Influence of the substrate nature on the peel strength of the assemblies between rigid and flexible substrates

strength were performed in a special conditioned chamber with 50% relative humidity, temperature of 25°C.

Taking into account the practical applications, the peel strength tests were done on a large variety of substrates, both on the same type of materials (flexible/flexible, rigid/rigid) and on hybrid materials (flexible/rigid).

The results on the peel strength revealed the following aspects:

- the contact time is the most important factor that influences the peel strength. The performances of the system based on polychloroprene rubber are superior than those of hybrid acrylic adhesive. After 10 days contact time, the strength of the assembly between Al2024T_3 and flexible PVC for the polychloroprene rubber adhesive reaches the value of 2.6 kN/m and tends to become constant. The peel strength of the hybrid acrylic adhesive reaches the value of 1.46 kN/m. This difference could be attributed to the high crystallization rate, high sticking character and high substrate adherence of the polychloroprene rubber (adhesive or mixed breaking);
- the contact pressure influences the peel strength (fig.2). The superior performances were observed also for the polychloroprene rubber adhesives;
- the substrate nature also influences the peel strength both for the assemblies between flexible PVC and rigid substrate (fig.3) and for the rigid substrates (fig.4). In all

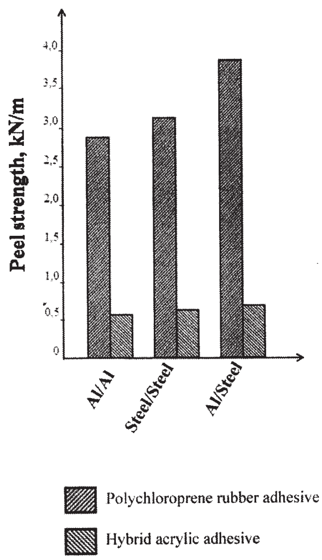

Fig.4. Influence of the rigid substrate nature on the peel strength; contact pressure 4N/cm²; 10 days contact time

the cases, the strengths of the assemblies based on hybrid acrylic adhesives are inferior to the polychloroprene rubber adhesive, but they are of the same order.

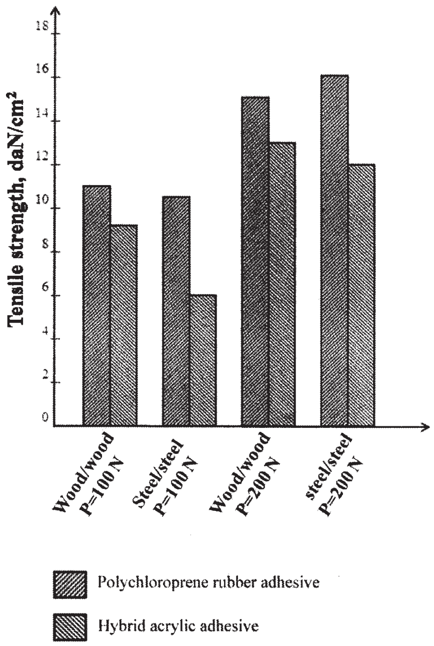

Fig.5. Dependence of the shear strengths on the substrate nature; contact pressure 4N/cm^2; 10 days contact time

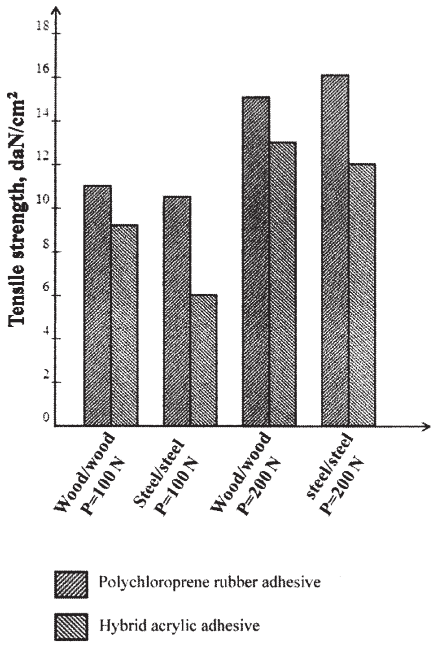

Fig.6. Influence of the substrate nature and pressure on the tensile strength; 10 days contact time

Table 4
VALUES OF THE ADHESION WORK (W_a), SCATTERING WORK (W_S) AND WETTING WORK (W_u)

No.	Substrate	Polychloroprene rubber adhesive			Hybrid acrylic adhesive		
		W_{a1}, erg/cm^2	W_{S1}, erg/cm^2	W_{u1}, erg/cm^2	W_{a2}, erg/cm^2	W_{S2}, erg/cm^2	W_{u2}, erg/cm^2
1	Textolite	47.23	-12.045	17.593	33.6	-28.963	2.325
2	Royalite (PVC)	46.00	-13.237	16.402	33.45	-29.129	2.159
3	Polymethyl methacrylate	44.70	-14.571	15.068	33.25	-29.317	1.971
4	Aluminium	47.00	-12.300	17.339	36.70	-25.838	5.450
5	Duralumin 2024T$_3$	45.10	-14.191	15.448	36.00	-26.610	4.678
6	Steel	43.36	-15.922	13.717	31.70	-30.884	0.404

The peel strength is practically independent on the substrate nature for the hybrid acrylic adhesive meaning a 100% cohesive breaking.

The shear strengths of the adhesive assemblies were determined on rigid substrates. The contact time and the contact pressure influence the values of the shear strengths. Superior results were obtained for the adhesive systems based on polychloroprene rubber. The results for the shear strength are shown in figure 5. Significant differences between the values of the shear strengths are observed for the 2 types of adhesives. The polychloroprene rubber has a better substrate adherence as compared to the hybrid acrylic adhesive. In this case, the value of the shear strength is independent on the substrate nature (100% cohesive breaking).

The comparison between the tensile strengths of the assemblies realized with the two adhesives systems on wood and steel samples revealed the influence of the substrate nature and contact pressure (fig.6).

The tensile tests have shown the superior adhesive performances of the systems based on polychloroprene rubber.

To obtain supplementary information on the performances of the adhesives systems the values of the contact angle and superficial tensions were determined.

The following parameters were determined:

- the adhesion work defined as the work required to separate the liquid and solid phase or the negative free energy associated to the adhesion between the liquid and solid phase according to Young-Dupre equation [22-23];

$$W_a = \gamma_L(1+\cos\theta) \qquad (2)$$

- the scattering work defined as the negative free energy associated to the scattering of the liquid onto the solid surface, according to equation [22]:

$$W_S = \gamma(\cos\theta - 1) \qquad (3)$$

- the wetting work:

$$W_u = \gamma_L \cdot \cos\theta \qquad (4)$$

The obtained results are shown in table 4. The analysis of the above presented data has revealed the superior performances of the polychloroprene adhesives and the dependence of these adhesives on the substrate nature. Therefore, the experimental data on the performances of the adhesive 2 systems are confirmed.

Conclusions

The comparative studies on the adhesive performances of polychloroprene rubber and hybrid acrylic adhesives have shown major differences and the significant role of the contact time, contact pressure and substrate nature upon the peel, shear and tensile strengths. Evaluation of the adhesion work, scattering work and wetting work confirmed the experimental results on the differences between the performances of the two adhesive systems.

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